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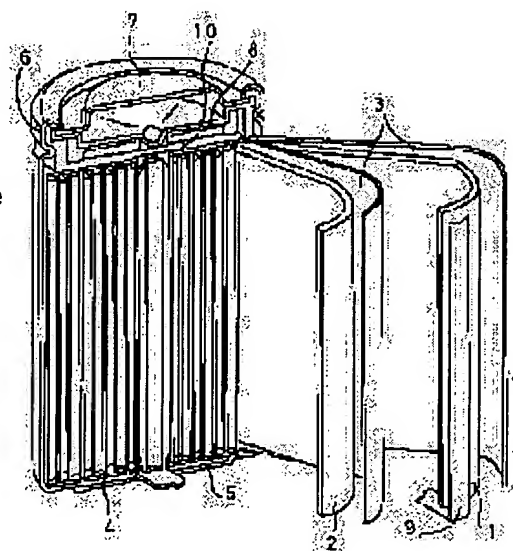
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## (54) MANUFACTURE OF NONAQUEOUS ELECTROLYTE SECONDARY BATTERY

### (57)Abstract:

**PURPOSE:** To provide a secondary battery with nonaqueous electrolyte in which the positive electrolyte active material is used with good effectiveness and which exerts a battery capacity to well suit the used amount of the positive electrode active material.

**CONSTITUTION:** A negative electrode 1 is fabricated using a negative electrode active material which is a carbonic substance capable of doping and dedoping with lithium, while a positive electrode 2 is made with a positive electrode active material which is a composite oxide of lithium transition metal. These electrodes 1, 2 are put in battery set to accomplish the intended battery, wherein the negative electrode is previously doped with lithium in an amount corresponding to irreversible capacity prior to the battery set. This permits the negative electrode of the resultant battery to contain lithium in the amount corresponding to the irreversible capacity already at the time of completion, so that the lithium doped in the charging process is not apparently consumed for setting off the irreversible capacity.



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CLAIMS

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[Claim(s)]

[Claim 1] A negative electrode is produced by making into a negative-electrode active material the carbon material in which the dope and \*\* dope of a lithium are possible. After producing a positive electrode on the other hand by making a lithium transition-metals multiple oxide into a positive active material, Make these negative electrodes and a positive electrode counter through separator, and they are contained with a cell can in this state. The manufacture method of the nonaqueous electrolyte rechargeable battery characterized by doping the lithium of the irreversible capacity by which a \*\* dope is not carried out even if it dopes to the carbon material of a negative electrode beforehand, before facing pouring in the electrolytic solution into this cell can, and assembling a cell and assembling a cell.

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[Translation done.]

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to an improvement of the use efficiency of a positive active material especially about the manufacture method of the nonaqueous electrolyte rechargeable battery using the carbon material in which the dope and \*\* dope of a lithium are possible as a negative-electrode active material.

[0002]

[Description of the Prior Art] In recent years, to be high-energy density is demanded also from the rechargeable battery which highly-efficient-izing of electronic equipment, a miniaturization, and portable-ization progress, and is used for these electronic equipment by progress of electronic technology.

[0003] Conventionally, as a rechargeable battery used for these electronic equipment, although solution system cells, such as a nickel cadmium battery and a lead cell, are used, these cells have a discharge potential inadequate for it being low and obtaining a high energy density.

[0004] Then, research and development of the nonaqueous electrolyte rechargeable battery which uses lithium multiple oxides, such as a lithium cobalt multiple oxide, as a positive active material are done recently, using a lithium, a lithium alloy, or the matter in which the dope and \*\* dope of a lithium ion like a carbon material are possible as a negative-electrode active material. This nonaqueous electrolyte rechargeable battery is expensive, and has a high energy density, self-discharge also has few cell voltages, and they are excellent in the cycle property.

[0005] In order to manufacture such a nonaqueous electrolyte rechargeable battery, a negative electrode and a positive electrode are produced as follows first. that is, a negative electrode distributes a powdered negative-electrode active material, for example, carbon-material powder, to a solvent with a binder -- making -- a negative electrode -- a mixture -- a paint is prepared and it produces by applying this to a negative-electrode charge collector and a positive electrode distributes a powdered lithium transition-metals multiple oxide to a solvent with an electric conduction agent and a binder too -- making -- a positive electrode -- a mixture -- a paint is prepared and it produces by applying this to a positive-electrode charge collector Thus, the cell group of the negative electrode and positive electrode which were produced is carried out.

[0006] In order to assemble a cell, this negative electrode and a positive electrode are made to counter through separator, and it contains with a cell can in this state. And the electrolytic solution is poured in into the above-mentioned cell can, and a cell is completed by sealing with a cell lid.

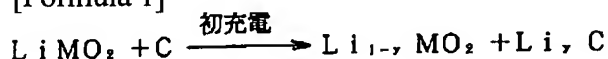
[0007]

[Problem(s) to be Solved by the Invention] By the way, the lithium doped by the carbon material by charge cannot usually carry out the \*\* dope of all by electric discharge. It is QR about the amount of lithiums in which a \*\* dope is carried out by QT and next electric discharge in the amount of lithiums doped by the initial charge. It is  $QT-QR=Q_i$  if it carries out.  $Q_i$  computed It will remain in a carbon material as an irreversible capacity also after electric discharge.

[0008] For example, the cell reaction at the time of using a carbon material C as a negative-electrode active material, and using LiMO<sub>2</sub> (however, M being transition metals) as a positive active material is shown in \*\* 1 and \*\* 2.

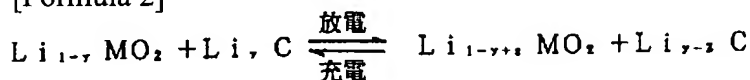
[0009]

[Formula 1]



[0010]

[Formula 2]



[0011] first, initial-charge process shows to \*\* 1 -- as -- LiMO<sub>2</sub> from -- y -- Li of an amount -- a \*\* dope -- carrying out -- a carbon material C -- y -- Li of an amount is doped

[0012] However, in a next electric discharge process, as shown in \*\* 2, the \*\* dope only of the Li of the amount which z Becomes among Li(s) doped by the carbon material C is carried out, and Li of the amount which becomes y-z remains in a carbon material C. and -- the charge-and-discharge process from a degree -- z -- Li of an amount -- a cell reaction -- involving -- consequent -- LiMO<sub>2</sub> from -- it was supplied -- y-z -- Li of an amount will become useless

[0013] Thus, by the cell produced by the old method, for the irreversible capacity which does not participate in this cell reaction, the use efficiency of a positive active material is low, and the cell capacity corresponding to the amount of the positive active material used is not obtained. For this reason, on the occasion of a cell design, it is necessary to set up the amount of positive active materials which foresaw this irreversible capacity beforehand, and there are problems, like material cost starts.

[0014] Then, this invention is proposed in view of such the conventional actual condition, and the use efficiency of a positive active material is high, and it aims at offering the manufacture method of a nonaqueous electrolyte rechargeable battery that the cell capacity corresponding to the amount of the positive active material used is obtained.

[0015]

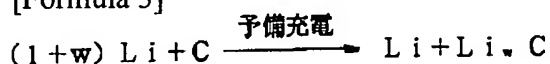
[Means for Solving the Problem] In order to attain the above-mentioned purpose, the nonaqueous electrolyte rechargeable battery of this invention The negative electrode produced considering the carbon material in which the dope and \*\* dope of a lithium are possible as a negative-electrode active material, It faces pouring in the electrolytic solution into this cell can, and assembling a cell, after making the positive electrode produced considering the lithium transition-metals multiple oxide as a positive active material counter through separator and containing it with a cell can in this state. at the production process of a negative electrode It is characterized by doping beforehand the lithium of the irreversible capacity by which a \*\* dope is not carried out even if it dopes to a carbon material.

[0016] Here, when a cell is constructed in the positive electrode which consists of a negative electrode which consists of the carbon material concerned, and a lithium transition-metals multiple oxide, the irreversible capacity of the lithium in a carbon material is initial-charge process, and is the capacity of the lithium which a \*\* dope is not carried out from a negative electrode in a subsequent electric discharge process among the lithiums doped by the negative electrode with the \*\* dope of the lithium from a positive electrode, but remains in a negative electrode as it is.

[0017] By the cell by which the lithium of this irreversible capacity carried out the cell group of the negative electrode by which the preliminary dope was carried out, and was produced, since the negative electrode has already had the lithium of irreversible capacity, it has not been said that the lithium which carried out the \*\* dope from the positive electrode, and was doped by the negative electrode in initial-charge process will be consumed although irreversible capacity is buried further. Or it is the grade which can be disregarded even if it is. Therefore, in a next electric discharge process, the \*\* dope of all the abbreviation is carried out from a negative electrode, and the lithium doped by this initial charge can

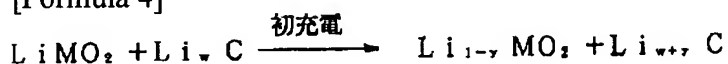
participate in a cell reaction also in this following charge-and-discharge process further. Therefore, the cell capacity corresponding to the amount of the positive active material used will be obtained.

[0018] It is [0019] when the above effect is explained using the cell-reaction formula of \*\* 3 --izing 5.  
[Formula 3]



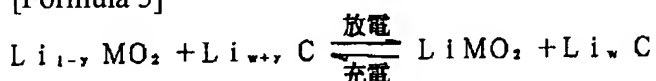
[0020]

[Formula 4]



[0021]

[Formula 5]



[0022] As shown in \*\* 3, the preliminary dope of the Li of the irreversible capacity equivalent w is carried out beforehand at the carbon material C of a negative electrode.

[0023] thus, when an initial charge is performed on the cell produced by carrying out the cell group of the negative electrode which carried out the preliminary dope of the Li, it is shown in it at \*\* 4 -- as -- LiMO<sub>2</sub> of a positive electrode from -- y -- Li of an amount -- a \*\* dope -- carrying out -- a carbon material C -- further -- y -- Li of an amount is doped Consequently, the lithium total amount of dopes of a carbon material C becomes w+y.

[0024] Then, since the irreversible capacity of a carbon material C is consumed by Li of the amount which was already doped in preliminary dope process and w Becoming as shown in \*\* 5 if it discharges, the \*\* dope of all the Li(s) that Li is not consumed although this irreversible capacity is buried further, and are equivalent to the amount y of dopes in the above-mentioned initial-charge process is carried out from a carbon material C.

[0025] And also in the charge-and-discharge process from a degree, all Li(s) equivalent to the amount y of dopes in this initial-charge process can participate in a cell reaction. namely, LiMO<sub>2</sub> from -- Li which carried out the \*\* dope will be used effectively

[0026]

[Function] A cell is manufactured by making a carbon material into a negative-electrode active material, producing a negative electrode, producing a positive electrode and on the other hand, carrying out the cell group of these negative electrodes and the positive electrode by making a lithium transition-metals multiple oxide into a positive active material.

[0027] In this invention, it faces manufacturing a cell in this way, and before carrying out a cell group to the carbon material of the above-mentioned negative electrode, the lithium of irreversible capacity is doped beforehand. By the cell by which the lithium of irreversible capacity carried out the cell group of the negative electrode by which the preliminary dope was carried out, and was produced, since the negative electrode has already had the lithium of irreversible capacity, it has not been said that the lithium which carried out the \*\* dope from the positive electrode, and was doped by the negative electrode in initial-charge process will be consumed although irreversible capacity is buried further. Therefore, in a next electric discharge process, the \*\* dope of all the abbreviation is carried out from a negative electrode, and the lithium doped by this initial charge can participate in a cell reaction also in the following charge-and-discharge process further. Therefore, the cell capacity corresponding to the amount of the positive active material used is obtained. Thereby, improvement in the use efficiency of a positive active material can be aimed at.

[0028]

[Example] The nonaqueous electrolyte rechargeable battery which makes a carbon material a negative-electrode active material, and makes a lithium transition-metals multiple oxide a positive active material

is manufactured as follows.

[0029] first, a negative electrode distributes a powdered carbon material to a solvent with a binder -- making -- a negative electrode -- a mixture -- a paint is prepared and it produces by applying this to a negative-electrode charge collector and a positive electrode distributes a powdered lithium transition-metals multiple oxide to a solvent with an electric conduction agent and a binder too -- making -- a positive electrode -- a mixture -- a paint is prepared and it produces by applying this to a positive-electrode charge collector And the cell group of the negative electrode and positive electrode which were produced by doing in this way is carried out.

[0030] In order to assemble a cell, this negative electrode and a positive electrode are made to counter through separator, and it contains with a cell can in this state. And after pouring in the electrolytic solution into the above-mentioned cell can, it seals with a cell lid.

[0031] In addition, the irreversible capacity of the lithium in a carbon material can be measured as follows, for example. That is, the cell group of the negative electrode which consists of the carbon material concerned with which the lithium is not doped is carried out, the cell for preliminary experiment is produced, an initial charge is performed about this cell, and it is the initial-charge capacity QT. It measures. The afterdischarge is performed and it is service capacity QR. It measures. This initial-charge capacity QT Shell service capacity QR The value and  $QT - QR = Q_i$  which were deducted It is equivalent to the lithium irreversible capacity in a carbon material.

[0032] Moreover, after the preliminary dope of the lithium to a carbon material produces a negative electrode by making a carbon material into a negative-electrode active material, it can be performed by using a lithium electrode for a counter electrode and charging this negative electrode in the electrolytic solution.

[0033] In addition, in the above manufacture method, the carbon material used as a negative-electrode active material and the lithium transition-metals multiple oxide used as a positive active material usually have each usable thing used on the occasion of manufacture of this kind of nonaqueous electrolyte rechargeable battery.

[0034] As a carbon material, pyrolytic carbons, corks (pitch coke, a needle coke, petroleum coke, etc.), graphite, glassy carbons, an organic high-molecular-compound baking object (that which calcinated phenol resin, the furan resin, etc. at suitable temperature, and carbonized them), a carbon fiber, activated carbon, a graphite, etc. are mentioned.

[0035] On the other hand, as a positive active material, the multiple oxide (however,  $0.05 \leq x \leq 1.10$   $0 < y < 1$ ) of  $\text{Li}_x \text{CoO}_2$ ,  $\text{Li}_x \text{NiO}_2$ ,  $\text{Li}_x \text{Ni}_{1-y} \text{Co}_y \text{O}_2$ , etc. is mentioned. The above-mentioned multiple oxide uses the carbonate of a lithium, cobalt, and nickel as a start raw material, and is obtained by mixing according to composition and calcinating these carbonates by the 600 degrees C - 1000 degrees C temperature requirement under oxygen existence atmosphere. In addition, a start raw material is not limited to a carbonate, but can be compounded similarly from a hydroxide and an oxide. Moreover, as a positive active material,  $\text{Li}_y \text{Mn}_2 \text{O}_4$  ( $0.05 \leq y \leq 2$ ) and  $\text{Li}_x \text{MnO}_2$  ( $0.05 \leq x \leq 1$ ) are also usable.

[0036] As the electrolytic solution, lithium salt is used as an electrolyte and the nonaqueous electrolyte which makes it come to dissolve this in an organic solvent is used, for example.

[0037] Especially as an organic solvent, although not limited, independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, gamma-butyl lactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, a sulfolane, an acetonitrile, diethyl carbonate, and dipropyl carbonate, are usable.

[0038] As an electrolyte,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{Li}(\text{C}_6 \text{H}_5)_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{CH}_3 \text{SO}_3 \text{Li}$ ,  $\text{CF}_3 \text{SO}_3 \text{Li}$ , etc. are usable.

[0039] Hereafter, the concrete example of this invention is explained based on an experimental result.

[0040] The composition of the nonaqueous electrolyte rechargeable battery produced by example 1 this example is shown in drawing 1. In this example, the nonaqueous electrolyte rechargeable battery of such composition was created as follows.

[0041] First, the positive electrode 2 was produced as follows.

[0042] A lithium carbonate and cobalt carbonate were mixed so that it might be set to Li/Co(mole ratio)

=1, among air, it calcinated at the temperature of 900 degrees C for 5 hours, and the positive active material ( $\text{LiCoO}_2$ ) was compounded.

[0043] As a result of performing X diffraction measurement about this positive active material, it is  $\text{LiCoO}_2$  of a JCPDS card. Well in agreement.

[0044] thus, obtained  $\text{LiCoO}_2$  95 % of the weight of powder, and 5 % of the weight of lithium carbonates -- mixing -- 91 % of the weight of this mixture -- further -- as electric conduction material -- as 6 % of the weight of graphite, and a binder -- 3 % of the weight of polyvinylidene fluorides -- mixing -- a positive electrode -- a mixture is prepared and it distributes to a N-methyl-2-pyrrolidone -- making -- a positive electrode -- a mixture -- it considered as the slurry

[0045] and this positive electrode -- a mixture -- the positive electrode 2 was produced by applying a slurry to both sides of the band-like aluminum foil used as a positive-electrode charge collector, and pressing it with the roller-press machine after dryness

[0046] The negative electrode 1 was produced as follows.

[0047] The petroleum pitch was used for the start raw material, after introducing the functional group which contains oxygen in this 10 to 20% and carrying out it (the so-called oxygen bridge formation), among inert gas, it calcinated at the temperature of 1000 degrees C, and the difficulty graphitized-carbon material of the property near a glassy carbon was obtained.

[0048] As a result of performing X diffraction measurement about this carbon material, the spacing of a field (002) was 3.76 and true specific gravity was 1.58.

[0049] as 90 % of the weight of this carbon material, and a binder -- 10 % of the weight of polyvinylidene fluorides -- mixing -- a negative electrode -- a mixture -- preparing -- a N-methyl-2-pyrrolidone -- distributing -- a negative electrode -- a mixture -- it considered as the slurry

[0050] this negative electrode -- a mixture -- the slurry was applied to both sides of the band-like copper foil used as a negative-electrode charge collector, and the negative electrode 1 was produced by pressing with the roller-press machine after dryness

[0051] Thus, the lithium electrode was used for the counter electrode, in the electrolytic solution, preliminary charge was performed to the produced negative electrode, and the lithium of 110mAh(s) was doped per 1g of carbon materials to it. In addition, this amount of dopes is an equivalent for the irreversible capacity for which it asked by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which carried out the cell group of the negative electrode, and produced it, without carrying out preliminary charge, and was then measured. Initial-charge capacity was a 500 mAh/g-carbon material, and service capacity was a 390 mAh/g-carbon material.

[0052] The laminating of the band-like positive electrode 2 produced as mentioned above and the band-like negative electrode 1 was carried out through the microporosity polypropylene film with a thickness of 25 micrometers it is thin to separator 3, it whirled by winding around a swirl type many times, and the mold electrode was produced.

[0053] And after inserting an electric insulating plate 4 in the pars basilaris ossis occipitalis of the iron cell can 5 which performed nickel plating, the above-mentioned whorl type electrode was contained. And in order to take current collection of a negative electrode, the end of the negative-electrode lead 9 made from nickel was stuck to the negative electrode 1 by pressure, and the other end was welded to the cell can 5. On the other hand, in order to take current collection of a positive electrode, the end of the positive-electrode lead 10 made from aluminum was attached in the positive electrode 2, and the other end was welded to the cell lid 7 with which the explosion-proof valve 8 which intercepts current according to cell internal pressure was attached.

[0054] Next, it is  $\text{LiPF}_6$  in this cell can 5 to the mixed solvent of propylene carbonate 50 capacity % and diethyl carbonate 50 capacity %. The electrolytic solution in which it makes it come to dissolve by the concentration which becomes 1 mol/l was poured in. And the cell lid 7 was fixed by closing the cell can 5 through the insulating obturation gasket 6 which applied asphalt, and the cylindrical cell with a diameter [ of 14mm ] and a height of 50mm was produced.

[0055] Charge and discharge were performed about the cell produced as mentioned above.



Consequently, by charging the electric capacity of a 390 mAh/g-carbon material in initial-charge process, a cell serves as a full charge, the service capacity of a 385 mAh/g-carbon material is obtained in a next electric discharge process, and it is \*\*\*\*. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 98.7%.

[0056] The nonaqueous electrolyte rechargeable battery was produced like the example 1 except not performing preliminary charge to example of comparison 1 negative electrode.

[0057] And charge and discharge were performed about the produced cell. Consequently, unless it charged the electric capacity of a 500 mAh/g-carbon material in initial-charge process, a cell did not become a full charge, but in a next electric discharge process, only the service capacity of a 385 mAh/g-carbon material was obtained to this charge capacity. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with  $385 / 500 = 0.770$ , i.e., 77.0%.

[0058] As mentioned above, when the result of an example 1 and the example 1 of comparison is compared, the initial-charge-and-discharge efficiency of the cell of the example 1 of comparison in which preliminary charge is not performed to a negative electrode to the initial-charge-and-discharge efficiency of the cell of an example 1 in which preliminary charge was performed being 98.7% is 77.0% and a low. From this, the negative electrode which consists of difficulty graphitized-carbon material understands that it is effective to carry out the preliminary dope of the lithium before a cell assembly, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0059] The nonaqueous electrolyte rechargeable battery was created like the example 1 to the negative electrode before the cell assembly except carrying out the preliminary dope of the lithium of 100mAh(s) per 1g of carbon materials, using a furfuryl-alcohol-resin baking object as an example 2 negative-electrode active material. In addition, this amount of dopes is an equivalent for the irreversible capacity for which it asked by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which carried out the cell group of the negative electrode, and produced it like the case of an example 1, without carrying out preliminary charge, and was then measured. Initial-charge capacity was a 450 mAh/g-carbon material, and service capacity was a 350 mAh/g-carbon material.

[0060] And charge and discharge were performed about the produced cell. Consequently, by charging the electric capacity of a 350 mAh/g-carbon material in initial-charge process, a cell serves as a full charge and the service capacity of a 349 mAh/g-carbon material can be obtained in a next electric discharge process. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 99.7%.

[0061] The nonaqueous electrolyte rechargeable battery was produced like the example 2 except not performing preliminary charge to example of comparison 2 negative electrode.

[0062] And charge and discharge were performed about the produced cell. Consequently, if electric capacity of a 450 mAh/g-carbon material is not charged in initial-charge process, a cell will not serve as a full charge but only the service capacity of a 350 mAh/g-carbon material will be obtained in a next electric discharge process to this charge capacity. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with  $350 / 450 = 0.778$ , i.e., 77.8%.

[0063] As mentioned above, when the result of an example 2 and the example 2 of comparison is compared, the initial-charge-and-discharge efficiency of the cell of the example 2 of comparison in which preliminary charge is not performed to a negative electrode to the initial-charge-and-discharge efficiency of the cell of an example 2 in which preliminary charge was performed being 99.7% is 77.8% and a low. This shows that it is effective to carry out the preliminary dope of the lithium before a cell assembly at a negative electrode when using a furfuryl-alcohol-resin baking object as a negative-electrode active material, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0064] The nonaqueous electrolyte rechargeable battery was created like the example 1 to the negative

electrode before the cell assembly except carrying out the preliminary dope of the lithium of 65mAh(s) per 1g of carbon materials, using corks as an example 3 negative-electrode active material. In addition, this amount of dopes is an irreversible capacity considerable amount calculated by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which carried out the cell group of the negative electrode, and produced it like the case of an example 1, without carrying out preliminary charge, and was then measured. Initial-charge capacity was a 350 mAh/g-carbon material, and service capacity was a 285 mAh/g-carbon material.

[0065] And charge and discharge were performed about the created cell. Consequently, by charging the electric capacity of a 285 mAh/g-carbon material in initial-charge process, a cell serves as a full charge and the service capacity of a 284 mAh/g-carbon material can be obtained in a next electric discharge process. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 99.6%.

[0066] The nonaqueous electrolyte rechargeable battery was created like the example 3 except not performing preliminary charge to example of comparison 3 negative electrode.

[0067] And charge and discharge were performed about the produced cell. Consequently, if electric capacity of a 350 mAh/g-carbon material is not charged in initial-charge process, a cell will not serve as a full charge but only the service capacity of a 285 mAh/g-carbon material will be obtained in a next electric discharge process to this charge capacity. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with  $285 / 350 = 0.814$ , i.e., 81.4%.

[0068] As mentioned above, when the result of an example 3 and the example 3 of comparison is compared, the initial-charge-and-discharge efficiency of the cell of the example 3 of comparison in which preliminary charge is not performed to a negative electrode to the initial-charge-and-discharge efficiency of the cell of an example 3 in which preliminary charge was performed being 99.6% is 81.4% and a low. This shows that it is effective to carry out the preliminary dope of the lithium before a cell assembly at a negative electrode when using corks as a negative-electrode active material, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0069] The nonaqueous electrolyte rechargeable battery was created like the example 1 to the negative electrode except carrying out the preliminary dope of the lithium of 62mAh(s) per 1g of carbon materials before a cell assembly, using graphite material as an example 4 negative-electrode active material. In addition, this amount of dopes is an irreversible capacity considerable amount calculated by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which did not carry out, but carried out the cell group of the preliminary charge to the negative electrode, and produced it to it like the case of an example 1, and was then measured. Initial-charge capacity was a 294 mAh/g-carbon material, and service capacity was a 232 mAh/g-carbon material.

[0070] And charge and discharge were performed about the created cell. Consequently, by charging the electric capacity of a 232 mAh/g-carbon material in initial-charge process, a cell serves as a full charge and the service capacity of a 230 mAh/g-carbon material can be obtained in a next electric discharge process. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 99.1%.

[0071] The nonaqueous electrolyte rechargeable battery was created like the example 4 except not performing preliminary charge to example of comparison 4 negative electrode.

[0072] About the created cell, when charge and discharge are performed, if electric capacity of a 294 mAh/g-carbon material is not charged in initial-charge process, a cell will not serve as a full charge but only the service capacity of a 232 mAh/g-carbon material will be obtained in a next electric discharge process to this charge capacity. The initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of this data to the above-mentioned cell is  $232 / 294 = 0.789$ , i.e., 78.9%.

[0073] As mentioned above, when the result of an example 4 and the example 4 of comparison is compared, for the cell of the example 4 of comparison by which, as for the cell of the example 4 which performed preliminary charge to the negative electrode, initial-charge-and-discharge efficiency does not perform preliminary charge to being 99.1%, initial-charge-and-discharge efficiency is 78.9% and a

low. This shows that it is effective to carry out the preliminary dope of the lithium before a cell assembly at a negative electrode when using graphite material as a negative-electrode active material, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0074] In addition, although the case where whirl as an electrode and a mold electrode is used is made into the example in the above example, when other electrode configurations, for example, a plane-area layer type electrode, are used, demonstrating the effect that this invention is the same cannot be overemphasized.

[0075]

[Effect of the Invention] So that clearly also from the above explanation by the manufacture method of the nonaqueous electrolyte rechargeable battery of this invention Produce a negative electrode by making into a negative-electrode active material the carbon material in which the dope and \*\* dope of a lithium are possible, produce a positive electrode by making a lithium transition-metals multiple oxide into a positive active material, and it faces carrying out the cell group of these negative electrodes and the positive electrode, and manufacturing a cell. Since the lithium of irreversible capacity is beforehand doped to the negative electrode before carrying out a cell group, the lithium doped by the negative electrode with the \*\* dope of the lithium from a positive electrode in initial-charge process in the completed cell is not consumed although irreversible capacity is buried further. Therefore, a positive active material is used efficiently and the nonaqueous electrolyte rechargeable battery which demonstrates the cell capacity corresponding to the amount of the positive active material used can be manufactured.

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TECHNICAL FIELD

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[Industrial Application] this invention relates to an improvement of the use efficiency of a positive active material especially about the manufacture method of the nonaqueous electrolyte rechargeable battery using the carbon material in which the dope and \*\* dope of a lithium are possible as a negative-electrode active material.

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PRIOR ART

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[Description of the Prior Art] In recent years, to be high-energy density is demanded also from the rechargeable battery which highly-efficient-izing of electronic equipment, a miniaturization, and portable-ization progress, and is used for these electronic equipment by progress of electronic technology.

[0003] Conventionally, as a rechargeable battery used for these electronic equipment, although solution system cells, such as a nickel cadmium battery and a lead cell, are used, these cells have a discharge potential inadequate for it being low and obtaining a high energy density.

[0004] Then, research and development of the nonaqueous electrolyte rechargeable battery which uses lithium multiple oxides, such as a lithium cobalt multiple oxide, as a positive active material are done recently, using a lithium, a lithium alloy, or the matter in which the dope and \*\* dope of a lithium ion like a carbon material are possible as a negative-electrode active material. This nonaqueous electrolyte rechargeable battery is expensive, and has a high energy density, self-discharge also has few cell voltages, and they are excellent in the cycle property.

[0005] In order to manufacture such a nonaqueous electrolyte rechargeable battery, a negative electrode and a positive electrode are produced as follows first. that is, a negative electrode distributes a powdered negative-electrode active material, for example, carbon-material powder, to a solvent with a binder -- making -- a negative electrode -- a mixture -- a paint is prepared and it produces by applying this to a negative-electrode charge collector and a positive electrode distributes a powdered lithium transition-metals multiple oxide to a solvent with an electric conduction agent and a binder too -- making -- a positive electrode -- a mixture -- a paint is prepared and it produces by applying this to a positive-electrode charge collector. Thus, the cell group of the negative electrode and positive electrode which were produced is carried out.

[0006] In order to assemble a cell, this negative electrode and a positive electrode are made to counter through separator, and it contains with a cell can in this state. And the electrolytic solution is poured in into the above-mentioned cell can, and a cell is completed by sealing with a cell lid.

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EFFECT OF THE INVENTION

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[Effect of the Invention] By the manufacture method of the nonaqueous electrolyte rechargeable battery of this invention, it is so that clearly also from the above explanation. Produce a negative electrode by making into a negative-electrode active material the carbon material in which the dope and \*\* dope of a lithium are possible, produce a positive electrode by making a lithium transition-metals multiple oxide into a positive active material, and it faces carrying out the cell group of these negative electrodes and the positive electrode, and manufacturing a cell. Since the lithium of irreversible capacity is beforehand doped to the negative electrode before carrying out a cell group, the lithium doped by the negative electrode with the \*\* dope of the lithium from a positive electrode in initial-charge process in the completed cell is not consumed although irreversible capacity is buried further. Therefore, a positive active material is used efficiently and the nonaqueous electrolyte rechargeable battery which demonstrates the cell capacity corresponding to the amount of the positive active material used can be manufactured.

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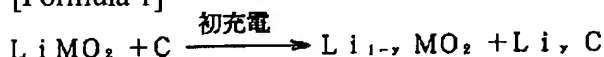
## TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] By the way, the lithium doped by the carbon material by charge cannot usually carry out the \*\* dope of all by electric discharge. It is QR about the amount of lithiums in which a \*\* dope is carried out by QT and next electric discharge in the amount of lithiums doped by the initial charge. It is  $QT - QR = Qi$  if it carries out.  $Qi$  computed It will remain in a carbon material as an irreversible capacity also after electric discharge.

[0008] For example, the cell reaction at the time of using a carbon material C as a negative-electrode active material, and using  $LiMO_2$  (however, M being transition metals) as a positive active material is shown in \*\* 1 and \*\* 2.

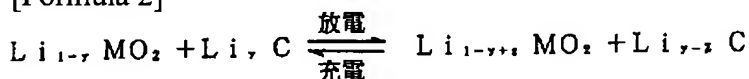
[0009]

[Formula 1]



[0010]

[Formula 2]



[0011] first, initial-charge process shows to \*\* 1 -- as --  $LiMO_2$  from -- y -- Li of an amount -- a \*\* dope -- carrying out -- a carbon material C -- y -- Li of an amount is doped

[0012] However, in a next electric discharge process, as shown in \*\* 2, the \*\* dope only of the Li of the amount which z Becomes among Li(s) doped by the carbon material C is carried out, and Li of the amount which becomes y-z remains in a carbon material C. and -- the charge-and-discharge process from a degree -- z -- Li of an amount -- a cell reaction -- involving -- consequent --  $LiMO_2$  from -- it was supplied -- y-z -- Li of an amount will become useless

[0013] Thus, by the cell produced by the old method, for the irreversible capacity which does not participate in this cell reaction, the use efficiency of a positive active material is low, and the cell capacity corresponding to the amount of the positive active material used is not obtained. For this reason, on the occasion of a cell design, it is necessary to set up the amount of positive active materials which foresaw this irreversible capacity beforehand, and there are problems, like material cost starts.

[0014] Then, this invention is proposed in view of such the conventional actual condition, and the use efficiency of a positive active material is high, and it aims at offering the manufacture method of a nonaqueous electrolyte rechargeable battery that the cell capacity corresponding to the amount of the positive active material used is obtained.

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## MEANS

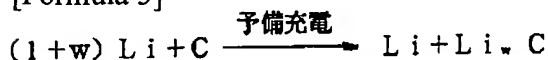
[Means for Solving the Problem] In order to attain the above-mentioned purpose, the nonaqueous electrolyte rechargeable battery of this invention The negative electrode produced considering the carbon material in which the dope and \*\* dope of a lithium are possible as a negative-electrode active material, It faces pouring in the electrolytic solution into this cell can, and assembling a cell, after making the positive electrode produced considering the lithium transition-metals multiple oxide as a positive active material counter through separator and containing it with a cell can in this state. at the production process of a negative electrode It is characterized by doping beforehand the lithium of the irreversible capacity by which a \*\* dope is not carried out even if it dopes to a carbon material.

[0016] Here, when a cell is constructed in the positive electrode which consists of a negative electrode which consists of the carbon material concerned, and a lithium transition-metals multiple oxide, the irreversible capacity of the lithium in a carbon material is initial-charge process, and is the capacity of the lithium which a \*\* dope is not carried out from a negative electrode in a subsequent electric discharge process among the lithiums doped by the negative electrode with the \*\* dope of the lithium from a positive electrode, but remains in a negative electrode as it is.

[0017] By the cell by which the lithium of this irreversible capacity carried out the cell group of the negative electrode by which the preliminary dope was carried out, and was produced, since the negative electrode has already had the lithium of irreversible capacity, it has not been said that the lithium which carried out the \*\* dope from the positive electrode, and was doped by the negative electrode in initial-charge process will be consumed although irreversible capacity is buried further. Or it is the grade which can be disregarded even if it is. Therefore, in a next electric discharge process, the \*\* dope of all the abbreviation is carried out from a negative electrode, and the lithium doped by this initial charge can participate in a cell reaction also in this following charge-and-discharge process further. Therefore, the cell capacity corresponding to the amount of the positive active material used will be obtained.

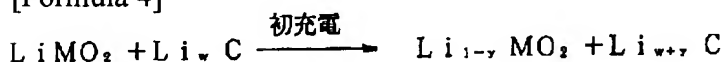
[0018] If the above effect is explained using the cell-reaction formula of \*\* 3 --izing 5 [0019]

[Formula 3]



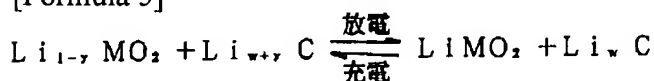
[0020]

[Formula 4]



[0021]

[Formula 5]



[0022] As shown in \*\* 3, the preliminary dope of the Li of the irreversible capacity equivalent w is



carried out beforehand at the carbon material C of a negative electrode.

[0023] thus, when an initial charge is performed on the cell produced by carrying out the cell group of the negative electrode which carried out the preliminary dope of the Li, it is shown in it at \*\* 4 -- as --  $\text{LiMO}_2$  of a positive electrode from -- y -- Li of an amount -- a \*\* dope -- carrying out -- a carbon material C -- further -- y -- Li of an amount is doped Consequently, the lithium total amount of dopes of a carbon material C becomes  $w+y$ .

[0024] Then, since the irreversible capacity of a carbon material C is consumed by Li of the amount which was already doped in preliminary dope process and w Becoming as shown in \*\* 5 if it discharges, the \*\* dope of all the Li(s) that Li is not consumed although this irreversible capacity is buried further, and are equivalent to the amount y of dopes in the above-mentioned initial-charge process is carried out from a carbon material C.

[0025] And also in the charge-and-discharge process from a degree, all Li(s) equivalent to the amount y of dopes in this initial-charge process can participate in a cell reaction. namely,  $\text{LiMO}_2$  from -- Li which carried out the \*\* dope will be used effectively

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OPERATION

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[Function] A cell is manufactured by making a carbon material into a negative-electrode active material, producing a negative electrode, producing a positive electrode and on the other hand, carrying out the cell group of these negative electrodes and the positive electrode by making a lithium transition-metals multiple oxide into a positive active material.

[0027] In this invention, it faces manufacturing a cell in this way, and before carrying out a cell group to the carbon material of the above-mentioned negative electrode, the lithium of irreversible capacity is doped beforehand. By the cell by which the lithium of irreversible capacity carried out the cell group of the negative electrode by which the preliminary dope was carried out, and was produced, since the negative electrode has already had the lithium of irreversible capacity, it has not been said that the lithium which carried out the \*\* dope from the positive electrode, and was doped by the negative electrode in initial-charge process will be consumed although irreversible capacity is buried further. Therefore, in a next electric discharge process, the \*\* dope of all the abbreviation is carried out from a negative electrode, and the lithium doped by this initial charge can participate in a cell reaction also in the following charge-and-discharge process further. Therefore, the cell capacity corresponding to the amount of the positive active material used is obtained. Thereby, improvement in the use efficiency of a positive active material can be aimed at.

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## EXAMPLE

[Example] The nonaqueous electrolyte rechargeable battery which makes a carbon material a negative-electrode active material, and makes a lithium transition-metals multiple oxide a positive active material is manufactured as follows.

[0029] first, a negative electrode distributes a powdered carbon material to a solvent with a binder -- making -- a negative electrode -- a mixture -- a paint is prepared and it produces by applying this to a negative-electrode charge collector and a positive electrode distributes a powdered lithium transition-metals multiple oxide to a solvent with an electric conduction agent and a binder too -- making -- a positive electrode -- a mixture -- a paint is prepared and it produces by applying this to a positive-electrode charge collector And the cell group of the negative electrode and positive electrode which were produced by doing in this way is carried out.

[0030] In order to assemble a cell, this negative electrode and a positive electrode are made to counter through separator, and it contains with a cell can in this state. And after pouring in the electrolytic solution into the above-mentioned cell can, it seals with a cell lid.

[0031] In addition, the irreversible capacity of the lithium in a carbon material can be measured as follows, for example. That is, the cell group of the negative electrode which consists of the carbon material concerned with which the lithium is not doped is carried out, the cell for preliminary experiment is produced, an initial charge is performed about this cell, and it is the initial-charge capacity QT. It measures. The afterdischarge is performed and it is service capacity QR. It measures. This initial-charge capacity QT Shell service capacity QR The value and  $QT - QR = Q_i$  which were deducted It is equivalent to the lithium irreversible capacity in a carbon material.

[0032] Moreover, after the preliminary dope of the lithium to a carbon material produces a negative electrode by making a carbon material into a negative-electrode active material, it can be performed by using a lithium electrode for a counter electrode and charging this negative electrode in the electrolytic solution.

[0033] In addition, in the above manufacture method, the carbon material used as a negative-electrode active material and the lithium transition-metals multiple oxide used as a positive active material usually have each usable thing used on the occasion of manufacture of this kind of nonaqueous electrolyte rechargeable battery.

[0034] As a carbon material, pyrolytic carbons, corks (pitch coke, a needle coke, petroleum coke, etc.), graphite, glassy carbons, an organic high-molecular-compound baking object (that which calcinated phenol resin, the furan resin, etc. at suitable temperature, and carbonized them), a carbon fiber, activated carbon, a graphite, etc. are mentioned.

[0035] On the other hand, as a positive active material, the multiple oxide (however,  $0.05 \leq x \leq 1.10$   $0 < y < 1$ ) of  $\text{Li}_x \text{CoO}_2$ ,  $\text{Li}_x \text{NiO}_2$ ,  $\text{Li}_x \text{Ni}_y \text{Co}_{1-y} \text{O}_2$ , etc. is mentioned. The above-mentioned multiple oxide uses the carbonate of a lithium, cobalt, and nickel as a start raw material, and is obtained by mixing according to composition and calcinating these carbonates by the 600 degrees C - 1000 degrees C temperature requirement under oxygen existence atmosphere. In addition, a start raw material is not limited to a carbonate, but can be compounded similarly from a hydroxide and an oxide. Moreover, as a

positive active material,  $\text{Li}_y\text{Mn}_2\text{O}_4$  ( $0.05 \leq y \leq 2$ ) and  $\text{Li}_x\text{MnO}_2$  ( $0.05 \leq x \leq 1$ ) are also usable.

[0036] As the electrolytic solution, lithium salt is used as an electrolyte and the nonaqueous electrolyte which makes it come to dissolve this in an organic solvent is used, for example.

[0037] Especially as an organic solvent, although not limited, independent or two or more kinds of mixed solvents, such as propylene carbonate, ethylene carbonate, 1, 2-dimethoxyethane, gamma-butyrolactone, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, a sulfolane, an acetonitrile, diethyl carbonate, and dipropyl carbonate, are usable.

[0038] As an electrolyte,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{Li}(\text{C}_6\text{H}_5)_4$ ,  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{CH}_3\text{SO}_3\text{Li}$ ,  $\text{CF}_3\text{SO}_3\text{Li}$ , etc. are usable.

[0039] Hereafter, the concrete example of this invention is explained based on an experimental result.

[0040] The composition of the nonaqueous electrolyte rechargeable battery produced by example 1 this example is shown in drawing 1. In this example, the nonaqueous electrolyte rechargeable battery of such composition was created as follows.

[0041] First, the positive electrode 2 was produced as follows.

[0042] A lithium carbonate and cobalt carbonate were mixed so that it might be set to  $\text{Li}/\text{Co}$  (mole ratio) = 1, among air, it calcinated at the temperature of 900 degrees C for 5 hours, and the positive active material ( $\text{LiCoO}_2$ ) was compounded.

[0043] As a result of performing X diffraction measurement about this positive active material, it is  $\text{LiCoO}_2$  of a JCPDS card. Well in agreement.

[0044] thus, obtained  $\text{LiCoO}_2$  95 % of the weight of powder, and 5 % of the weight of lithium carbonates -- mixing -- 91 % of the weight of this mixture -- further -- as electric conduction material -- as 6 % of the weight of graphite, and a binder -- 3 % of the weight of polyvinylidene fluorides -- mixing -- a positive electrode -- a mixture is prepared and it distributes to a N-methyl-2-pyrrolidone -- making -- a positive electrode -- a mixture -- it considered as the slurry

[0045] and this positive electrode -- a mixture -- the positive electrode 2 was produced by applying a slurry to both sides of the band-like aluminum foil used as a positive-electrode charge collector, and pressing it with the roller-press machine after dryness

[0046] The negative electrode 1 was produced as follows.

[0047] The petroleum pitch was used for the start raw material, after introducing the functional group which contains oxygen in this 10 to 20% and carrying out it (the so-called oxygen bridge formation), among inert gas, it calcinated at the temperature of 1000 degrees C, and the difficulty graphitized-carbon material of the property near a glassy carbon was obtained.

[0048] As a result of performing X diffraction measurement about this carbon material, the spacing of a field (002) was 3.76 and true specific gravity was 1.58.

[0049] as 90 % of the weight of this carbon material, and a binder -- 10 % of the weight of polyvinylidene fluorides -- mixing -- a negative electrode -- a mixture -- preparing -- a N-methyl-2-pyrrolidone -- distributing -- a negative electrode -- a mixture -- it considered as the slurry

[0050] this negative electrode -- a mixture -- the slurry was applied to both sides of the band-like copper foil used as a negative-electrode charge collector, and the negative electrode 1 was produced by pressing with the roller-press machine after dryness

[0051] Thus, the lithium electrode was used for the counter electrode, in the electrolytic solution, preliminary charge was performed to the produced negative electrode, and the lithium of 110mAh(s) was doped per 1g of carbon materials to it. In addition, this amount of dopes is an equivalent for the irreversible capacity for which it asked by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which carried out the cell group of the negative electrode, and produced it, without carrying out preliminary charge, and was then measured. Initial-charge capacity was a 500 mAh/g-carbon material, and service capacity was a 390 mAh/g-carbon material.

[0052] The laminating of the band-like positive electrode 2 produced as mentioned above and the band-like negative electrode 1 was carried out through the microporosity polypropylene film with a thickness of 25 micrometers it is thin to separator 3, it whirled by winding around a swirl type many times, and the

mold electrode was produced.

[0053] And after inserting an electric insulating plate 4 in the pars basilaris ossis occipitalis of the iron cell can 5 which performed nickel plating, the above-mentioned whorl type electrode was contained. And in order to take current collection of a negative electrode, the end of the negative-electrode lead 9 made from nickel was stuck to the negative electrode 1 by pressure, and the other end was welded to the cell can 5. On the other hand, in order to take current collection of a positive electrode, the end of the positive-electrode lead 10 made from aluminum was attached in the positive electrode 2, and the other end was welded to the cell lid 7 with which the explosion-proof valve 8 which intercepts current according to cell internal pressure was attached.

[0054] Next, it is LiPF<sub>6</sub> in this cell can 5 to the mixed solvent of propylene carbonate 50 capacity % and diethyl carbonate 50 capacity %. The electrolytic solution in which it makes it come to dissolve by the concentration which becomes 1 mol/l was poured in. And the cell lid 7 was fixed by closing the cell can 5 through the insulating obturation gasket 6 which applied asphalt, and the cylindrical cell with a diameter [ of 14mm ] and a height of 50mm was produced.

[0055] Charge and discharge were performed about the cell produced as mentioned above. Consequently, by charging the electric capacity of a 390 mAh/g-carbon material in initial-charge process, a cell serves as a full charge, the service capacity of a 385 mAh/g-carbon material is obtained in a next electric discharge process, and it is \*\*\*\*. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 98.7%.

[0056] The nonaqueous electrolyte rechargeable battery was produced like the example 1 except not performing preliminary charge to example of comparison 1 negative electrode.

[0057] And charge and discharge were performed about the produced cell. Consequently, unless it charged the electric capacity of a 500 mAh/g-carbon material in initial-charge process, a cell did not become a full charge, but in a next electric discharge process, only the service capacity of a 385 mAh/g-carbon material was obtained to this charge capacity. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with  $385 / 500 = 0.770$ , i.e., 77.0%.

[0058] As mentioned above, when the result of an example 1 and the example 1 of comparison is compared, the initial-charge-and-discharge efficiency of the cell of the example 1 of comparison in which preliminary charge is not performed to a negative electrode to the initial-charge-and-discharge efficiency of the cell of an example 1 in which preliminary charge was performed being 98.7% is 77.0% and a low. From this, the negative electrode which consists of difficulty graphitized-carbon material understands that it is effective to carry out the preliminary dope of the lithium before a cell assembly, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0059] The nonaqueous electrolyte rechargeable battery was created like the example 1 to the negative electrode before the cell assembly except carrying out the preliminary dope of the lithium of 100mAh(s) per 1g of carbon materials, using a furfuryl-alcohol-resin baking object as an example 2 negative-electrode active material. In addition, this amount of dopes is an equivalent for the irreversible capacity for which it asked by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which carried out the cell group of the negative electrode, and produced it like the case of an example 1, without carrying out preliminary charge, and was then measured. Initial-charge capacity was a 450 mAh/g-carbon material, and service capacity was a 350 mAh/g-carbon material.

[0060] And charge and discharge were performed about the produced cell. Consequently, by charging the electric capacity of a 350 mAh/g-carbon material in initial-charge process, a cell serves as a full charge and the service capacity of a 349 mAh/g-carbon material can be obtained in a next electric discharge process. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 99.7%.

[0061] The nonaqueous electrolyte rechargeable battery was produced like the example 2 except not performing preliminary charge to example of comparison 2 negative electrode.

[0062] And charge and discharge were performed about the produced cell. Consequently, if electric capacity of a 450 mAh/g-carbon material is not charged in initial-charge process, a cell will not serve as a full charge but only the service capacity of a 350 mAh/g-carbon material will be obtained in a next electric discharge process to this charge capacity. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with  $350 / 450 = 0.778$ , i.e., 77.8%.

[0063] As mentioned above, when the result of an example 2 and the example 2 of comparison is compared, the initial-charge-and-discharge efficiency of the cell of the example 2 of comparison in which preliminary charge is not performed to a negative electrode to the initial-charge-and-discharge efficiency of the cell of an example 2 in which preliminary charge was performed being 99.7% is 77.8% and a low. This shows that it is effective to carry out the preliminary dope of the lithium before a cell assembly at a negative electrode when using a furfuryl-alcohol-resin baking object as a negative-electrode active material, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0064] The nonaqueous electrolyte rechargeable battery was created like the example 1 to the negative electrode before the cell assembly except carrying out the preliminary dope of the lithium of 65mAh(s) per 1g of carbon materials, using corks as an example 3 negative-electrode active material. In addition, this amount of dopes is an irreversible capacity considerable amount calculated by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which carried out the cell group of the negative electrode, and produced it like the case of an example 1, without carrying out preliminary charge, and was then measured. Initial-charge capacity was a 350 mAh/g-carbon material, and service capacity was a 285 mAh/g-carbon material.

[0065] And charge and discharge were performed about the created cell. Consequently, by charging the electric capacity of a 285 mAh/g-carbon material in initial-charge process, a cell serves as a full charge and the service capacity of a 284 mAh/g-carbon material can be obtained in a next electric discharge process. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 99.6%.

[0066] The nonaqueous electrolyte rechargeable battery was created like the example 3 except not performing preliminary charge to example of comparison 3 negative electrode.

[0067] And charge and discharge were performed about the produced cell. Consequently, if electric capacity of a 350 mAh/g-carbon material is not charged in initial-charge process, a cell will not serve as a full charge but only the service capacity of a 285 mAh/g-carbon material will be obtained in a next electric discharge process to this charge capacity. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with  $285 / 350 = 0.814$ , i.e., 81.4%.

[0068] As mentioned above, when the result of an example 3 and the example 3 of comparison is compared, the initial-charge-and-discharge efficiency of the cell of the example 3 of comparison in which preliminary charge is not performed to a negative electrode to the initial-charge-and-discharge efficiency of the cell of an example 3 in which preliminary charge was performed being 99.6% is 81.4% and a low. This shows that it is effective to carry out the preliminary dope of the lithium before a cell assembly at a negative electrode when using corks as a negative-electrode active material, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0069] The nonaqueous electrolyte rechargeable battery was created like the example 1 to the negative electrode except carrying out the preliminary dope of the lithium of 62mAh(s) per 1g of carbon materials before a cell assembly, using graphite material as an example 4 negative-electrode active material. In addition, this amount of dopes is an irreversible capacity considerable amount calculated by deducting service capacity from the initial-charge capacity which performed charge and discharge on the cell which did not carry out, but carried out the cell group of the preliminary charge to the negative electrode, and produced it to it like the case of an example 1, and was then measured. Initial-charge capacity was a 294 mAh/g-carbon material, and service capacity was a 232 mAh/g-carbon material.

[0070] And charge and discharge were performed about the created cell. Consequently, by charging the

electric capacity of a 232 mAh/g-carbon material in initial-charge process, a cell serves as a full charge and the service capacity of a 230 mAh/g-carbon material can be obtained in a next electric discharge process. From this data, the initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of the above-mentioned cell was computed with 99.1%.

[0071] The nonaqueous electrolyte rechargeable battery was created like the example 4 except not performing preliminary charge to example of comparison 4 negative electrode.

[0072] About the created cell, when charge and discharge are performed, if electric capacity of a 294 mAh/g-carbon material is not charged in initial-charge process, a cell will not serve as a full charge but only the service capacity of a 232 mAh/g-carbon material will be obtained in a next electric discharge process to this charge capacity. The initial-charge-and-discharge efficiency [(the amount of electric discharge)/(charge)] of this data to the above-mentioned cell is  $232 / 294 = 0.789$ , i.e., 78.9%.

[0073] As mentioned above, when the result of an example 4 and the example 4 of comparison is compared, for the cell of the example 4 of comparison by which, as for the cell of the example 4 which performed preliminary charge to the negative electrode, initial-charge-and-discharge efficiency does not perform preliminary charge to being 99.11%, initial-charge-and-discharge efficiency is 78.9% and a low. This shows that it is effective to carry out the preliminary dope of the lithium before a cell assembly at a negative electrode when using graphite material as a negative-electrode active material, when aiming at improvement in the initial-charge-and-discharge efficiency of a cell.

[0074] In addition, although the case where whirl as an electrode and a mold electrode is used is made into the example in the above example, when other electrode configurations, for example, a plane-area layer type electrode, are used, demonstrating the effect that this invention is the same cannot be overemphasized.

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[Translation done.]

\* NOTICES \*

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3. In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the development showing an example of the nonaqueous electrolyte rechargeable battery of this invention.

[Description of Notations]

- 1 Negative Electrode
- 2 Positive Electrode
- 3 Separator
- 4 Electric Insulating Plate
- 5 Cell Can
- 6 Obturation Gasket
- 7 Cell Lid
- 8 Explosion-proof Valve
- 9 Negative-Electrode Lead
- 10 Positive-Electrode Lead

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\* NOTICES \*

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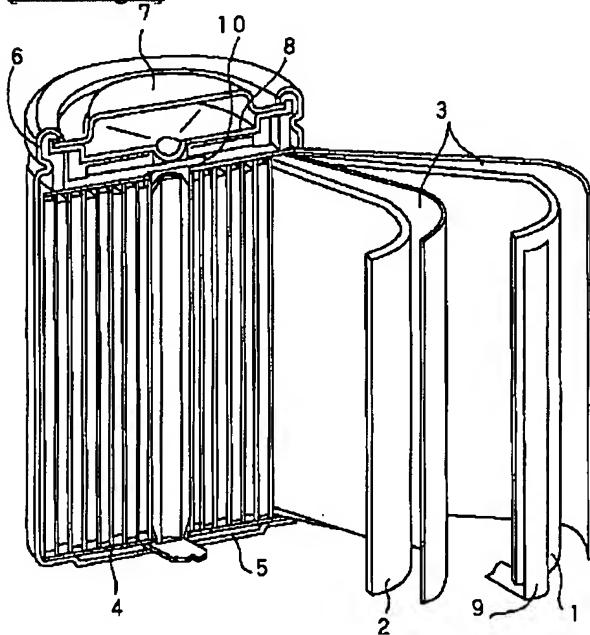
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DRAWINGS

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[Drawing 1]



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[Translation done.]

## 書誌

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- (19)【発行国】日本国特許庁（ＪＰ）  
(12)【公報種別】公開特許公報（Ａ）  
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(51)【国際特許分類第６版】

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                    4/04            A  
                    4/58  
                    4/96            H

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## 要約

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- (57)【要約】

【構成】 リチウムのドーブ・脱ドーブが可能な炭素材料を負極活物質として負極１を作製し、リチウム遷移金属複合酸化物を正極活物質として正極２を作製し、これら負極１，正極２を電池組して電池を製造するに際して、電池組する前に予め負極に不可逆容量相当分のリチウムをドーブしておく。

【効果】 完成した電池において、既に負極が不可逆容量相当分のリチウムを有しているの

で、さらに充電過程でドーピングされたリチウムが不可逆容量を埋めるのに消費されることが見かけ上ない。したがって、正極活物質の効率良く利用され、正極活物質の使用量に見合った電池容量を発揮する非水電解液二次電池が製造できる。

#### 請求の範囲

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##### 【特許請求の範囲】

【請求項1】 リチウムのドーピング・脱ドーピングが可能な炭素材料を負極活物質として負極を作製し、一方、リチウム遷移金属複合酸化物を正極活物質として正極を作製した後、これら負極、正極を、セパレータを介して対向させ、この状態で電池缶に収納し、該電池缶内に電解液を注入して電池を組み立てるに際し、電池を組み立てる前に予め、負極の炭素材料に、ドーピングしても脱ドーピングされない不可逆容量相当分のリチウムをドーピングしておくことを特徴とする非水電解液二次電池の製造方法。

#### 詳細な説明

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##### 【発明の詳細な説明】

##### 【0001】

【産業上の利用分野】 本発明は、リチウムのドーピング・脱ドーピングが可能な炭素材料を負極活物質として用いる非水電解液二次電池の製造方法に関し、特に正極活物質の利用効率の改善に関する。

##### 【0002】

【従来の技術】 近年、電子技術の進歩により、電子機器の高性能化、小型化、ポータブル化が進み、これら電子機器に使用される二次電池に対しても高エネルギー密度であることが要求されるようになっている。

【0003】 従来、これら電子機器に使用される二次電池としては、ニッケル・カドミウム電池や鉛電池等の水溶液系電池が用いられているが、これら電池は放電電位が低く、高いエネルギー密度を得るには不十分である。

【0004】 そこで、最近、リチウムやリチウム合金もしくは炭素材料のようなリチウムイオンのドーピング・脱ドーピングが可能な物質を負極活物質として用い、またリチウムコバルト複合酸化物等のリチウム複合酸化物を正極活物質として使用する非水電解液二次電池の研究・開発が行われている。この非水電解液二次電池は電池電圧が高く、高いエネルギー密度を有し、自己放電も少なく、かつサイクル特性に優れている。

【0005】 このような非水電解液二次電池を製造するには、まず負極、正極を次のようにして作製する。すなわち、負極は、粉末状の負極活物質、例えば炭素材料粉末をバインダーとともに溶媒に分散させて負極合剤塗料を調製し、これを負極集電体に塗布することで作製する。そして、正極は、やはり粉末状のリチウム遷移金属複合酸化物を導電剤、バインダーとともに溶剤に分散させて正極合剤塗料を調製し、これを正極集電体に塗布する

ことで作製する。このようにして作製された負極、正極を電池組する。

【0006】電池を組み立てるには、この負極、正極をセパレータを介して対向させ、この状態で電池缶に収納する。そして、上記電池缶内に電解液を注入し、電池蓋で密閉することで電池が完成する。

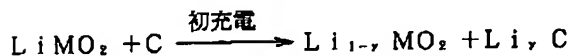
【0007】

【発明が解決しようとする課題】ところで、通常、充電によって炭素材料にドーピングされたリチウムは、放電によって全てを脱ドーピングさせることはできない。初充電によってドーピングされたリチウム量を $Q_T$ 、この後の放電によって脱ドーピングされるリチウム量を $Q_R$ とすると、 $Q_T - Q_R = Q_i$ で算出される $Q_i$ が放電後にも不可逆容量として炭素材料中に残存してしまう。

【0008】例えば、負極活物質として炭素材料Cを、正極活物質として $LiMO_x$ (但し、Mは遷移金属である)を用いた場合の電池反応を化1、化2に示す。

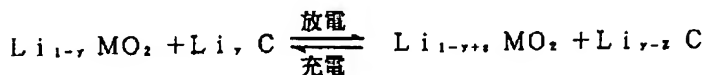
【0009】

【化1】



【0010】

【化2】



【0011】まず、初充電過程では、化1に示すように、 $LiMO_x$ から $y$ なる量の $Li$ が脱ドーピングし、炭素材料Cに $y$ なる量の $Li$ がドーピングされる。

【0012】しかし、この後の放電過程では、化2に示すように、炭素材料Cにドーピングされた $Li$ のうち $z$ なる量の $Li$ のみが脱ドーピングされ、 $y - z$ なる量の $Li$ が炭素材料Cに残存する。そして次からの充放電過程では、 $z$ なる量の $Li$ のみが電池反応に関与し、結果的に $LiMO_x$ から供給された $y - z$ なる量の $Li$ は無駄になってしまう。

【0013】このように、これまでの方法で作製された電池では、この電池反応に関与しない不可逆容量のため、正極活物質の利用効率が低く、正極活物質使用量に見合うだけの電池容量が得られない。このため、電池設計に際して、あらかじめこの不可逆容量を見越した正極活物質量を設定する必要がある、材料コストがかかる等の問題がある。

【0014】そこで、本発明は、このような従来の実情に鑑みて提案されたものであり、正極活物質の利用効率が高く、正極活物質の使用量に見合った電池容量が得られる非水電解液二次電池の製造方法を提供することを目的とする。

【0015】

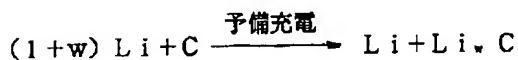
【課題を解決するための手段】上述の目的を達成するために、本発明の非水電解液二次電池は、リチウムのドーブ・脱ドーブが可能な炭素材料を負極活物質として作製された負極と、リチウム遷移金属複合酸化物を正極活物質として作製された正極を、セパレータを介して対向させ、この状態で電池缶に収納した後、該電池缶内に電解液を注入して電池を組み立てるに際し、負極の作製工程で、炭素材料に、ドーブしても脱ドーブされない不可逆容量相当分のリチウムを予めドーブしておくことを特徴とするものである。

【0016】ここで、炭素材料におけるリチウムの不可逆容量とは、当該炭素材料よりなる負極とリチウム遷移金属複合酸化物よりなる正極で電池を組んだ場合に、初充電過程で、正極からのリチウムの脱ドーブを伴って負極にドーブされたリチウムのうち、その後の放電過程で負極から脱ドーブされず、そのまま負極に残存するリチウムの容量である。

【0017】この不可逆容量相当分のリチウムが予備ドーブされた負極を電池組して作製された電池では、既に負極が不可逆容量相当分のリチウムを有していることから、初充電過程で、正極から脱ドーブし、負極にドーブされたリチウムが、さらに不可逆容量を埋めるのに消費されてしまうといったことがない。あるいはあっても無視できる程度である。したがって、この初充電でドーブされたリチウムは、この後の放電過程で略全てが負極から脱ドーブされ、さらにこの次の充放電過程においても電池反応に関与できる。したがって、正極活物質の使用量に見合った電池容量が得られることになる。

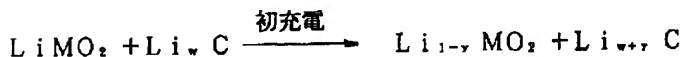
【0018】以上の効果を、化3～化5の電池反応式を用いて説明すると、【0019】

【化3】



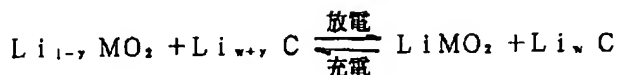
【0020】

【化4】



【0021】

【化5】



【0022】化3に示すように、負極の炭素材料Cには、予め不可逆容量相当分wのLiを予備ドーブしておく。

【0023】このようにLiを予備ドーブした負極を電池組して作製された電池に、初充電を行うと、化4に示すように、正極のLiMO<sub>2</sub>からyなる量のLiが脱ドーブし、炭素

材料Cにさらに $y$ なる量のLiがドーピングされる。その結果、炭素材料Cのリチウム総ドーピング量は、 $w + y$ になる。

【0024】その後、放電を行うと、化5に示すように、炭素材料Cの不可逆容量は既に予備ドーピング過程でドーピングされた $w$ なる量のLiによって消費されているので、さらにこの不可逆容量を埋めるのにLiが消費されることはなく、上記初充電過程でのドーピング量 $y$ に相当するLiは全て炭素材料Cから脱ドーピングされる。

【0025】そして次からの充放電過程でも、この初充電過程でのドーピング量 $y$ に相当するLiが全て電池反応に関与できる。すなわち、 $\text{LiMO}_2$ から脱ドーピングしたLiが、有効利用されることになる。

【0026】

【作用】電池は、炭素材料を負極活物質として負極を作製し、一方リチウム遷移金属複合酸化物を正極活物質として正極を作製し、これら負極、正極を電池組することで製造される。

【0027】本発明では、このように電池を製造するに際して、上記負極の炭素材料に、電池組する前に予め、不可逆容量相当分のリチウムをドーピングしておく。不可逆容量相当分のリチウムが予備ドーピングされた負極を電池組して作製された電池では、既に負極が不可逆容量相当分のリチウムを有していることから、初充電過程で、正極から脱ドーピングし、負極にドーピングされたリチウムが、さらに不可逆容量を埋めるのに消費されてしまうといったことがない。したがって、この初充電でドーピングされたリチウムは、この後の放電過程で略全てが負極から脱ドーピングされ、さらに次の充放電過程においても電池反応に関与できる。したがって、正極活物質の使用量に見合った電池容量が得られる。これにより、正極活物質の利用効率の向上を図ることができる。

【0028】

【実施例】炭素材料を負極活物質とし、リチウム遷移金属複合酸化物を正極活物質とする非水電解液二次電池は、以下のようにして製造される。

【0029】まず、負極は、粉末状の炭素材料をバインダーとともに溶媒に分散させて負極合剤塗料を調製し、これを負極集電体に塗布することで作製する。そして、正極は、やはり粉末状のリチウム遷移金属複合酸化物を導電剤、バインダーとともに溶剤に分散させて正極合剤塗料を調製し、これを正極集電体に塗布することで作製する。そして、このようにして作製された負極、正極を電池組する。

【0030】電池を組み立てるには、この負極、正極をセパレータを介して対向させ、この状態で電池缶に収納する。そして、上記電池缶内に電解液を注入した後、電池蓋で密閉する。

【0031】なお、炭素材料におけるリチウムの不可逆容量は、例えば、以下のようにして測定できる。すなわち、リチウムがドーピングされていない当該炭素材料よりなる負極を電池組して予備実験用の電池を作製し、この電池について初充電を行って初充電容量 $Q$ を測

定する。その後放電を行って放電容量 $Q_R$ を測定する。この初充電容量 $Q_T$ から放電容量 $Q_R$ を差し引いた値、 $Q_T - Q_R = Q_i$ が炭素材料におけるリチウム不可逆容量に相当する。

【0032】また、炭素材料へのリチウムの予備ドープは、炭素材料を負極活物質として負極を作製した後、この負極に、リチウム電極を対極に用いて電解液中で充電することで行うことができる。

【0033】なお、以上の製造方法において、負極活物質として用いる炭素材料、正極活物質として用いるリチウム遷移金属複合酸化物は、通常、この種の非水電解液二次電池の製造に際して用いられているものがいずれも使用可能である。

【0034】炭素材料としては、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、石油コークス等）、グラファイト類、ガラス状炭素類、有機高分子化合物焼成体（フェノール樹脂、フラン樹脂等を適当な温度で焼成し、炭素化したもの）、炭素繊維、活性炭、黒鉛等が挙げられる。

【0035】一方、正極活物質としては、 $Li_xCoO_2$ 、 $Li_xNiO_2$ 、 $Li_xNi_yCo_{1-y}O_2$ （但し、 $0.05 \leq x \leq 1.10$ 、 $0 < y < 1$ ）などの複合酸化物が挙げられる。上記複合酸化物は、例えばリチウム、コバルト、ニッケルの炭酸塩を出発原料とし、これら炭酸塩を組成に応じて混合し、酸素存在雰囲気下 $600^\circ\text{C} \sim 1000^\circ\text{C}$ の温度範囲で焼成することにより得られる。なお、出発原料は炭酸塩に限定されず、水酸化物、酸化物からも同様に合成可能である。また、正極活物質としては、 $Li_yMn_2O_4$ （ $0.05 \leq y \leq 2$ ）、 $Li_xMnO_2$ （ $0.05 \leq x \leq 1$ ）も使用可能である。

【0036】電解液としては、例えば、リチウム塩を電解質とし、これを有機溶媒に溶解させてなる非水電解液が用いられる。

【0037】有機溶媒としては、特に限定されるものではないが、プロピレンカーボネート、エチレンカーボネート、1,2-ジメトキシエタン、 $\gamma$ -ブチラクトン、テトラヒドロフラン、2-メチルテトラヒドロフラン、1,3-ジオキソラン、スルホラン、アセトニトリル、ジエチルカーボネート、ジプロピルカーボネート等の単独もしくは2種類以上の混合溶媒が使用可能である。

【0038】電解質としては、 $LiClO_4$ 、 $LiAsF_6$ 、 $LiPF_6$ 、 $LiBF_4$ 、 $LiB(C_6H_5)_4$ 、 $LiCl$ 、 $LiBr$ 、 $CH_3SO_3Li$ 、 $CF_3SO_3Li$ 等が使用可能である。

【0039】以下、本発明の具体的な実施例を実験結果に基づいて説明する。

【0040】実施例1本実施例で作製した非水電解液二次電池の構成を図1に示す。本実施例ではこのような構成の非水電解液二次電池を以下のようにして作成した。

【0041】まず、正極2は次のようにして作製した。

【0042】炭酸リチウムと炭酸コバルトを、 $Li/Co$ （モル比）=1となるように混合し、空气中、温度 $900^\circ\text{C}$ で5時間焼成して正極活物質（ $LiCoO_2$ ）を合成した。

【0043】この正極活物質についてX線回折測定を行った結果、JCPDSカードのL

LiCoO<sub>2</sub>と良く一致していた。

【0044】このようにして得られたLiCoO<sub>2</sub>粉末95重量%、炭酸リチウム5重量%を混合し、この混合物91重量%に、さらに導電材としてグラファイト6重量%、結着剤としてポリフッ化ビニリデン3重量%を混合して正極合剤を調製し、N-メチルー2-ピロリドンに分散させて正極合剤スラリーとした。

【0045】そして、この正極合剤スラリーを、正極集電体となる帯状のアルミニウム箔の両面に塗布し、乾燥後ローラプレス機で圧縮成形することで正極2を作製した。

【0046】負極1は次のようにして作製した。

【0047】出発原料に石油ピッチを用い、これに酸素を含む官能基を10～20%導入し(いわゆる酸素架橋)した後、不活性ガス中、温度1000℃で焼成してガラス状炭素に近い性質の難黒鉛化炭素材料を得た。

【0048】この炭素材料についてX線回折測定を行った結果、(002)面の面間隔は3.76、真比重は1.58であった。

【0049】この炭素材料90重量%、結着剤としてポリフッ化ビニリデン10重量%を混合して負極合剤を調製し、N-メチルー2-ピロリドンに分散して負極合剤スラリーとした。

【0050】この負極合剤スラリーを負極集電体となる帯状銅箔の両面に塗布し、乾燥後ローラプレス機で圧縮成形することで負極1を作製した。

【0051】このようにして作製された負極に、リチウム電極を対極に用いて電解液中で、予備充電を行い、炭素材料1g当たり110mAhのリチウムをドーブした。なお、このドーブ量は、負極を予備充電せずに電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当分である。初充電容量は500mAh/g-炭素材料、放電容量は390mAh/g-炭素材料であった。

【0052】以上のようにして作製された帯状正極2、帯状負極1を、セパレータ3となる厚さ25μmの微孔性ポリプロピレンフィルムを介して積層し、渦巻型に多数回巻回することで渦巻き型電極を作製した。

【0053】そして、ニッケルメッキを施した鉄製の電池缶5の底部に絶縁板4を挿入した後、上記渦巻き型電極を収納した。そして、負極の集電をとるためにニッケル製の負極リード9の一端を負極1に圧着し、他端を電池缶5に溶接した。一方、正極の集電をとるためにアルミニウム製の正極リード10の一端を正極2に取り付け、他端を電池内圧に応じて電流を遮断する防爆弁8が取り付けられた電池蓋7に溶接した。

【0054】次に、この電池缶5の中にプロピレンカーボネート50容量%とジエチルカーボネート50容量%の混合溶媒にLiPF<sub>6</sub>を1mol/lなる濃度で溶解させてなる電解液を注入した。そして、アスファルトを塗布した絶縁封口ガasket6を介して電池缶5をかしめることで電池蓋7を固定し、直径14mm、高さ50mmの円筒型電池を作製した。



【0055】以上のようにして作製した電池について充放電を行った。その結果、初充電過程では $390\text{mAh/g}$ —炭素材料の電気容量を充電することにより電池が満充電となり、この後の放電過程では $385\text{mAh/g}$ —炭素材料の放電容量が得られた。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は $98.7\%$ と算出された。

【0056】比較例1負極に予備充電を行わないこと以外は実施例1と同様にして非水電解液二次電池を作製した。

【0057】そして、作製した電池について充放電を行った。その結果、初充電過程では $500\text{mAh/g}$ —炭素材料の電気容量を充電しないと電池が満充電とならず、この充電容量に対してこの後の放電過程では $385\text{mAh/g}$ —炭素材料の放電容量しか得られなかった。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は $385/500=0.770$ 、すなわち $77.0\%$ と算出された。

【0058】以上、実施例1、比較例1の結果を比較すると、負極に予備充電を行った実施例1の電池の初充放電効率が $98.7\%$ であるのに対して、予備充電を行わない比較例1の電池の初充放電効率は $77.0\%$ と低い。このことから、難黒鉛化炭素材料よりなる負極に、電池組み立て前にリチウムを予備ドープしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0059】実施例2負極活物質としてフルフリルアルコール樹脂焼成体を用い、電池組み立て前に負極に炭素材料 $1\text{g}$ 当たり $100\text{mAh}$ のリチウムを予備ドープしておくこと以外は実施例1と同様にして非水電解液二次電池を作成した。なお、このドープ量は、実施例1の場合と同様、負極を予備充電せずに電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当分である。初充電容量は $450\text{mAh/g}$ —炭素材料、放電容量は $350\text{mAh/g}$ —炭素材料であった。

【0060】そして、作製した電池について、充放電を行った。その結果、初充電過程では、 $350\text{mAh/g}$ —炭素材料の電気容量を充電することにより電池が満充電となり、この後の放電過程では、 $349\text{mAh/g}$ —炭素材料の放電容量を得ることができる。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は $99.7\%$ と算出された。

【0061】比較例2負極に予備充電を行わないこと以外は実施例2と同様にして非水電解液二次電池を作製した。

【0062】そして、作製した電池について、充放電を行った。その結果、初充電過程では、 $450\text{mAh/g}$ —炭素材料の電気容量を充電しないと電池が満充電とならず、この充電容量に対して、この後の放電過程では $350\text{mAh/g}$ —炭素材料の放電容量しか得られない。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は $350/450=0.778$ 、すなわち $77.8\%$ と算出された。

【0063】以上、実施例2、比較例2の結果を比較すると、負極に予備充電を行った実

実施例2の電池の初充放電効率が99.7%であるのに対して、予備充電を行わない比較例2の電池の初充放電効率は77.8%と低い。このことから、フルフリルアルコール樹脂焼成体を負極活物質として用いる場合においても、電池組み立て前に、負極にリチウムを予備ドープしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0064】実施例3負極活物質としてコークス類を用い、電池組み立て前に負極に炭素材料1g当たり65mAhのリチウムを予備ドープしておくこと以外は実施例1と同様にして非水電解液二次電池を作成した。なお、このドープ量は、実施例1の場合と同様、負極を予備充電せずに電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当量である。初充電容量は350mAh/g-炭素材料、放電容量は285mAh/g-炭素材料であった。

【0065】そして、作成した電池について、充放電を行った。その結果、初充電過程では、285mAh/g-炭素材料の電気容量を充電することにより電池が満充電となり、この後の放電過程では、284mAh/g-炭素材料の放電容量を得ることができる。このデータから、上記電池の初充放電効率〔(放電量)/(充電量)〕は99.6%と算出された。

【0066】比較例3負極に予備充電を行わないこと以外は実施例3と同様にして非水電解液二次電池を作成した。

【0067】そして、作製した電池について、充放電を行った。その結果、初充電過程では、350mAh/g-炭素材料の電気容量を充電しないと電池が満充電とならず、この充電容量に対して、この後の放電過程では285mAh/g-炭素材料の放電容量しか得られない。このデータから、上記電池の初充放電効率〔(放電量)/(充電量)〕は $285/350=0.814$ 、すなわち81.4%と算出された。

【0068】以上、実施例3、比較例3の結果を比較すると、負極に予備充電を行った実施例3の電池の初充放電効率が99.6%であるのに対して、予備充電を行わない比較例3の電池の初充放電効率は81.4%と低い。このことから、コークス類を負極活物質として用いる場合においても、電池組み立て前に、負極にリチウムを予備ドープしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0069】実施例4負極活物質として黒鉛材料を用い、負極に対して、電池組み立て前に炭素材料1g当たり62mAhのリチウムを予備ドープすること以外は実施例1と同様にして非水電解液二次電池を作成した。なお、このドープ量は、実施例1の場合と同様、負極に予備充電を行わず電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当量である。初充電容量は294mAh/g-炭素材料、放電容量は232mAh/g-炭素材料であった。

【0070】そして、作成した電池について、充放電を行った。その結果、初充電過程では、232mAh/g-炭素材料の電気容量を充電することにより電池が満充電となり、

この後の放電過程では、 $230\text{mAh/g}$ 炭素材料の放電容量を得ることができる。このデータから、上記電池の初充放電効率〔（放電量）／（充電量）〕は $99.1\%$ と算出された。

【0071】比較例4負極に予備充電を行わないこと以外は実施例4と同様にして非水電解液二次電池を作成した。

【0072】作成した電池について、充放電を行ったところ、初充電過程では、 $294\text{mAh/g}$ 炭素材料の電気容量を充電しないと電池が満充電とならず、この充電容量に対して、この後の放電過程では $232\text{mAh/g}$ 炭素材料の放電容量しか得られない。このデータから、上記電池の初充放電効率〔（放電量）／（充電量）〕は $232/294=0.789$ ，すなわち $78.9\%$ である。

【0073】以上、実施例4，比較例4の結果を比較すると、負極に予備充電を行った実施例4の電池は初充放電効率が $99.11\%$ であるのに対して、予備充電を行わない比較例4の電池は初充放電効率が $78.9\%$ と低い。このことから、黒鉛材料を負極活物質として用いる場合においても、電池組み立て前に、負極にリチウムを予備ドーピングしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0074】なお、以上の実施例では、電極として渦巻き型電極を用いる場合を例にしているが、他の電極形状，例えば平面積層型の電極を用いた場合にも本発明が同様の効果を発揮することは言うまでもない。

#### 【0075】

【発明の効果】以上の説明からも明らかなように、本発明の非水電解液二次電池の製造方法では、リチウムのドーピング・脱ドーピングが可能な炭素材料を負極活物質として負極を作製し、リチウム遷移金属複合酸化物を正極活物質として正極を作製し、これら負極，正極を電池組して電池を製造するに際して、電池組する前に予め負極に不可逆容量相当分のリチウムをドーピングしておくので、完成した電池において初充電過程で、正極からのリチウムの脱ドーピングを伴って負極にドーピングされたリチウムがさらに不可逆容量を埋めるのに消費されることがない。したがって、正極活物質が効率良く利用され、正極活物質の使用量に見合った電池容量を発揮する非水電解液二次電池が製造できる。

#### 分野

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【産業上の利用分野】本発明は、リチウムのドーピング・脱ドーピングが可能な炭素材料を負極活物質として用いる非水電解液二次電池の製造方法に関し、特に正極活物質の利用効率の改善に関する。

#### 技術

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【従来の技術】近年、電子技術の進歩により、電子機器の高性能化，小型化，ポータブル化が進み、これら電子機器に使用される二次電池に対しても高エネルギー密度であること

が要求されるようになっている。

【0003】従来、これら電子機器に使用される二次電池としては、ニッケル・カドミウム電池や鉛電池等の水溶液系電池が用いられているが、これら電池は放電電位が低く、高いエネルギー密度を得るには不十分である。

【0004】そこで、最近、リチウムやリチウム合金もしくは炭素材料のようなリチウムイオンのドーブ・脱ドーブが可能な物質を負極活物質として用い、またリチウムコバルト複合酸化物等のリチウム複合酸化物を正極活物質として使用する非水電解液二次電池の研究・開発が行われている。この非水電解液二次電池は電池電圧が高く、高いエネルギー密度を有し、自己放電も少なく、かつサイクル特性に優れている。

【0005】このような非水電解液二次電池を製造するには、まず負極、正極を次のようにして作製する。すなわち、負極は、粉末状の負極活物質、例えば炭素材料粉末をバインダーとともに溶媒に分散させて負極合剤塗料を調製し、これを負極集電体に塗布することで作製する。そして、正極は、やはり粉末状のリチウム遷移金属複合酸化物を導電剤、バインダーとともに溶剤に分散させて正極合剤塗料を調製し、これを正極集電体に塗布することで作製する。このようにして作製された負極、正極を電池組する。

【0006】電池を組み立てるには、この負極、正極をセパレータを介して対向させ、この状態で電池缶に収納する。そして、上記電池缶内に電解液を注入し、電池蓋で密閉することで電池が完成する。

## 効果

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【発明の効果】以上の説明からも明らかなように、本発明の非水電解液二次電池の製造方法では、リチウムのドーブ・脱ドーブが可能な炭素材料を負極活物質として負極を作製し、リチウム遷移金属複合酸化物を正極活物質として正極を作製し、これら負極、正極を電池組して電池を製造するに際して、電池組する前に予め負極に不可逆容量相当分のリチウムをドーブしておくので、完成した電池において初充電過程で、正極からのリチウムの脱ドーブを伴って負極にドーブされたリチウムがさらに不可逆容量を埋めるのに消費されることがない。したがって、正極活物質が効率良く利用され、正極活物質の使用量に見合った電池容量を発揮する非水電解液二次電池が製造できる。

## 課題

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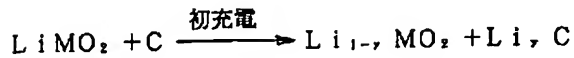
【発明が解決しようとする課題】ところで、通常、充電によって炭素材料にドーブされたリチウムは、放電によって全てを脱ドーブさせることはできない。初充電によってドーブされたリチウム量を $Q_T$ 、この後の放電によって脱ドーブされるリチウム量を $Q_R$ とすると、 $Q_T - Q_R = Q_i$ で算出される $Q_i$ が放電後にも不可逆容量として炭素材料中に残存してしまう。

【0008】例えば、負極物質として炭素材料Cを、正極活物質としてLiMQ（但し、

Mは遷移金属である)を用いた場合の電池反応を化1, 化2に示す。

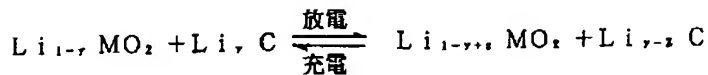
【0009】

【化1】



【0010】

【化2】



【0011】まず、初充電過程では、化1に示すように、 $\text{LiMO}_2$  から  $y$  なる量の  $\text{Li}$  が脱ドーブし、炭素材料  $\text{C}$  に  $y$  なる量の  $\text{Li}$  がドーブされる。

【0012】しかし、この後の放電過程では、化2に示すように、炭素材料  $\text{C}$  にドーブされた  $\text{Li}$  のうち  $z$  なる量の  $\text{Li}$  のみが脱ドーブされ、 $y-z$  なる量の  $\text{Li}$  が炭素材料  $\text{C}$  に残存する。そして次からの充放電過程では、 $z$  なる量の  $\text{Li}$  のみが電池反応に関与し、結果的に  $\text{LiMO}_2$  から供給された  $y-z$  なる量の  $\text{Li}$  は無駄になってしまう。

【0013】このように、これまでの方法で作製された電池では、この電池反応に関与しない不可逆容量のため、正極活物質の利用効率が低く、正極活物質使用量に見合うだけの電池容量が得られない。このため、電池設計に際して、あらかじめこの不可逆容量を見越した正極活物質量を設定する必要があり、材料コストがかかる等の問題がある。

【0014】そこで、本発明は、このような従来の実情に鑑みて提案されたものであり、正極活物質の利用効率が高く、正極活物質の使用量に見合った電池容量が得られる非水電解液二次電池の製造方法を提供することを目的とする。

手段

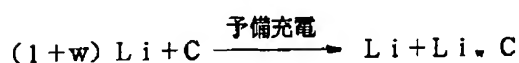
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【課題を解決するための手段】上述の目的を達成するために、本発明の非水電解液二次電池は、リチウムのドーブ・脱ドーブが可能な炭素材料を負極活物質として作製された負極と、リチウム遷移金属複合酸化物を正極活物質として作製された正極を、セパレータを介して対向させ、この状態で電池缶に収納した後、該電池缶内に電解液を注入して電池を組み立てるに際し、負極の作製工程で、炭素材料に、ドーブしても脱ドーブされない不可逆容量相当分のリチウムを予めドーブしておくことを特徴とするものである。

【0016】ここで、炭素材料におけるリチウムの不可逆容量とは、当該炭素材料よりなる負極とリチウム遷移金属複合酸化物よりなる正極で電池を組んだ場合に、初充電過程で、正極からのリチウムの脱ドーブを伴って負極にドーブされたリチウムのうち、その後の放電過程で負極から脱ドーブされず、そのまま負極に残存するリチウムの容量である。

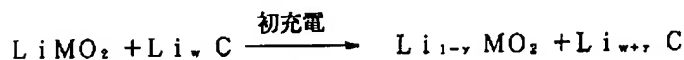
【0017】この不可逆容量相当分のリチウムが予備ドーピングされた負極を電池組して作製された電池では、既に負極が不可逆容量相当分のリチウムを有していることから、初充電過程で、正極から脱ドーピングし、負極にドーピングされたリチウムが、さらに不可逆容量を埋めるのに消費されてしまうといったことがない。あるいはあっても無視できる程度である。したがって、この初充電でドーピングされたリチウムは、この後の放電過程で略全てが負極から脱ドーピングされ、さらにこの次の充放電過程においても電池反応に関与できる。したがって、正極活物質の使用量に見合った電池容量が得られることになる。

【0018】以上の効果を、化3～化5の電池反応式を用いて説明すると、【0019】  
【化3】



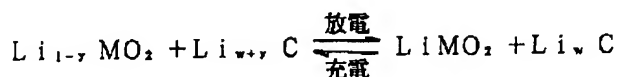
【0020】

【化4】



【0021】

【化5】



【0022】化3に示すように、負極の炭素材料Cには、予め不可逆容量相当分wのLiを予備ドーピングしておく。

【0023】このようにLiを予備ドーピングした負極を電池組して作製された電池に、初充電を行うと、化4に示すように、正極のLiMO<sub>2</sub>からyなる量のLiが脱ドーピングし、炭素材料Cにさらにyなる量のLiがドーピングされる。その結果、炭素材料Cのリチウム総ドーピング量は、w+yになる。

【0024】その後、放電を行うと、化5に示すように、炭素材料Cの不可逆容量は既に予備ドーピング過程でドーピングされたwなる量のLiによって消費されているので、さらにこの不可逆容量を埋めるのにLiが消費されることはなく、上記初充電過程でのドーピング量yに相当するLiは全て炭素材料Cから脱ドーピングされる。

【0025】そして次からの充放電過程でも、この初充電過程でのドーピング量yに相当するLiが全て電池反応に関与できる。すなわち、LiMO<sub>2</sub>から脱ドーピングしたLiが、有効利用されることになる。

作用

【作用】電池は、炭素材料を負極活物質として負極を作製し、一方リチウム遷移金属複合酸化物を正極活物質として正極を作製し、これら負極、正極を電池組することで製造される。

【0027】本発明では、このように電池を製造するに際して、上記負極の炭素材料に、電池組する前に予め、不可逆容量相当分のリチウムをドーピングしておく。不可逆容量相当分のリチウムが予備ドーピングされた負極を電池組して作製された電池では、既に負極が不可逆容量相当分のリチウムを有していることから、初充電過程で、正極から脱ドーピングし、負極にドーピングされたリチウムが、さらに不可逆容量を埋めるのに消費されてしまうといったことがない。したがって、この初充電でドーピングされたリチウムは、この後の放電過程で略全てが負極から脱ドーピングされ、さらに次の充放電過程においても電池反応に関与できる。したがって、正極活物質の使用量に見合った電池容量が得られる。これにより、正極活物質の利用効率の向上を図ることができる。

#### 実施例

【実施例】炭素材料を負極活物質とし、リチウム遷移金属複合酸化物を正極活物質とする非水電解液二次電池は、以下のようにして製造される。

【0029】まず、負極は、粉末状の炭素材料をバインダーとともに溶媒に分散させて負極合剤塗料を調製し、これを負極集電体に塗布することで作製する。そして、正極は、やはり粉末状のリチウム遷移金属複合酸化物を導電剤、バインダーとともに溶剤に分散させて正極合剤塗料を調製し、これを正極集電体に塗布することで作製する。そして、このようにして作製された負極、正極を電池組する。

【0030】電池を組み立てるには、この負極、正極をセパレータを介して対向させ、この状態で電池缶に収納する。そして、上記電池缶内に電解液を注入した後、電池蓋で密閉する。

【0031】なお、炭素材料におけるリチウムの不可逆容量は、例えば、以下のようにして測定できる。すなわち、リチウムがドーピングされていない当該炭素材料よりなる負極を電池組して予備実験用の電池を作製し、この電池について初充電を行って初充電容量 $Q_T$ を測定する。その後放電を行って放電容量 $Q_R$ を測定する。この初充電容量 $Q_T$ から放電容量 $Q_R$ を差し引いた値、 $Q_T - Q_R = Q_i$ が炭素材料におけるリチウム不可逆容量に相当する。

【0032】また、炭素材料へのリチウムの予備ドーピングは、炭素材料を負極活物質として負極を作製した後、この負極に、リチウム電極を対極に用いて電解液中で充電することで行うことができる。

【0033】なお、以上の製造方法において、負極活物質として用いる炭素材料、正極活物質として用いるリチウム遷移金属複合酸化物は、通常、この種の非水電解液二次電池の製造に際して用いられているものがいずれも使用可能である。

【0034】炭素材料としては、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、石油コークス等）、グラファイト類、ガラス状炭素類、有機高分子化合物焼成体（フェノール樹脂、フラン樹脂等を適当な温度で焼成し、炭素化したもの）、炭素繊維、活性炭、黒鉛等が挙げられる。

【0035】一方、正極活物質としては、 $\text{Li}_x\text{CoO}_2$ 、 $\text{Li}_x\text{NiO}_2$ 、 $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$ （但し、 $0.05 \leq x \leq 1.1$ 、 $0 < y < 1$ ）などの複合酸化物が挙げられる。上記複合酸化物は、例えばリチウム、コバルト、ニッケルの炭酸塩を出発原料とし、これら炭酸塩を組成に応じて混合し、酸素存在雰囲気下  $600^\circ\text{C} \sim 1000^\circ\text{C}$  の温度範囲で焼成することにより得られる。なお、出発原料は炭酸塩に限定されず、水酸化物、酸化物からも同様に合成可能である。また、正極活物質としては、 $\text{Li}_y\text{Mn}_2\text{O}_4$ （ $0.05 \leq y \leq 2$ ）、 $\text{Li}_x\text{MnO}_2$ （ $0.05 \leq x \leq 1$ ）も使用可能である。

【0036】電解液としては、例えば、リチウム塩を電解質とし、これを有機溶媒に溶解させてなる非水電解液が用いられる。

【0037】有機溶媒としては、特に限定されるものではないが、プロピレンカーボネート、エチレンカーボネート、1, 2-ジメトキシエタン、 $\gamma$ -ブチラクトン、テトラヒドロフラン、2-メチルテトラヒドロフラン、1, 3-ジオキソラン、スルホラン、アセトニトリル、ジエチルカーボネート、ジプロピルカーボネート等の単独もしくは2種類以上の混合溶媒が使用可能である。

【0038】電解質としては、 $\text{LiClO}_4$ 、 $\text{LiAsF}_6$ 、 $\text{LiPF}_6$ 、 $\text{LiBF}_4$ 、 $\text{LiB}(\text{C}_6\text{H}_5)_4$ 、 $\text{LiCl}$ 、 $\text{LiBr}$ 、 $\text{CH}_3\text{SO}_3\text{Li}$ 、 $\text{CF}_3\text{SO}_3\text{Li}$  等が使用可能である。

【0039】以下、本発明の具体的な実施例を実験結果に基づいて説明する。

【0040】実施例1 本実施例で作製した非水電解液二次電池の構成を図1に示す。本実施例ではこのような構成の非水電解液二次電池を以下のようにして作成した。

【0041】まず、正極2は次のようにして作製した。

【0042】炭酸リチウムと炭酸コバルトを、 $\text{Li}/\text{Co}$ （モル比）=1となるように混合し、空气中、温度  $900^\circ\text{C}$  で5時間焼成して正極活物質（ $\text{LiCoO}_2$ ）を合成した。

【0043】この正極活物質についてX線回折測定を行った結果、JCPDSカードの $\text{LiCoO}_2$ と良く一致していた。

【0044】このようにして得られた $\text{LiCoO}_2$ 粉末95重量%、炭酸リチウム5重量%を混合し、この混合物91重量%に、さらに導電材としてグラファイト6重量%、結着剤としてポリフッ化ビニリデン3重量%を混合して正極合剤を調製し、N-メチル-2-ピロリドンに分散させて正極合剤スラリーとした。

【0045】そして、この正極合剤スラリーを、正極集電体となる帯状のアルミニウム箔の両面に塗布し、乾燥後ローラプレス機で圧縮成形することで正極2を作製した。

【0046】負極1は次のようにして作製した。



【0047】出発原料に石油ピッチを用い、これに酸素を含む官能基を10～20%導入し（いわゆる酸素架橋）した後、不活性ガス中、温度1000℃で焼成してガラス状炭素に近い性質の難黒鉛化炭素材料を得た。

【0048】この炭素材料についてX線回折測定を行った結果、(002)面の面間隔は3.76、真比重は1.58であった。

【0049】この炭素材料90重量%、結着剤としてポリフッ化ビニリデン10重量%を混合して負極合剤を調製し、N-メチル-2-ピロリドンに分散して負極合剤スラリーとした。

【0050】この負極合剤スラリーを負極集電体となる帯状銅箔の両面に塗布し、乾燥後ロープレスマシで圧縮成形することで負極1を作製した。

【0051】このようにして作製された負極に、リチウム電極を対極に用いて電解液中で、予備充電を行い、炭素材料1g当たり110mAhのリチウムをドーブした。なお、このドーブ量は、負極を予備充電せずに電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当分である。初充電容量は500mAh/g-炭素材料、放電容量は390mAh/g-炭素材料であった。

【0052】以上のようにして作製された帯状正極2、帯状負極1を、セパレータ3となる厚さ25μmの微孔性ポリプロピレンフィルムを介して積層し、渦巻型に多数回巻回することで渦巻き型電極を作製した。

【0053】そして、ニッケルメッキを施した鉄製の電池缶5の底部に絶縁板4を挿入した後、上記渦巻き型電極を収納した。そして、負極の集電をとるためにニッケル製の負極リード9の一端を負極1に圧着し、他端を電池缶5に溶接した。一方、正極の集電をとるためにアルミニウム製の正極リード10の一端を正極2に取り付け、他端を電池内圧に応じて電流を遮断する防爆弁8が取り付けられた電池蓋7に溶接した。

【0054】次に、この電池缶5の中にプロピレンカーボネート50容量%とジエチルカーボネート50容量%の混合溶媒にLiPF<sub>6</sub>を1mol/lなる濃度で溶解させてなる電解液を注入した。そして、アスファルトを塗布した絶縁封口ガasket6を介して電池缶5をかしめることで電池蓋7を固定し、直径14mm、高さ50mmの円筒型電池を作製した。

【0055】以上のようにして作製した電池について充放電を行った。その結果、初充電過程では390mAh/g-炭素材料の電気容量を充電することにより電池が満充電となり、この後の放電過程では385mAh/g-炭素材料の放電容量が得られた。このデータから、上記電池の初充放電効率〔(放電量)/(充電量)〕は98.7%と算出された。

【0056】比較例1負極に予備充電を行わないこと以外は実施例1と同様にして非水電解液二次電池を作製した。

【0057】そして、作製した電池について充放電を行った。その結果、初充電過程では500mAh/g-炭素材料の電気容量を充電しないと電池が満充電とならず、この充電

容量に対してこの後の放電過程では $385\text{mAh/g}$ —炭素材料の放電容量しか得られなかった。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は $385/500=0.770$ ，すなわち $77.0\%$ と算出された。

【0058】以上、実施例1，比較例1の結果を比較すると、負極に予備充電を行った実施例1の電池の初充放電効率が $98.7\%$ であるのに対して、予備充電を行わない比較例1の電池の初充放電効率は $77.0\%$ と低い。このことから、難黒鉛化炭素材料よりなる負極に、電池組み立て前にリチウムを予備ドープしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0059】実施例2負極活物質としてフルフリルアルコール樹脂焼成体を用い、電池組み立て前に負極に炭素材料 $1\text{g}$ 当たり $100\text{mAh}$ のリチウムを予備ドープしておくこと以外は実施例1と同様にして非水電解液二次電池を作成した。なお、このドープ量は、実施例1の場合と同様、負極を予備充電せずに電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当分である。初充電容量は $450\text{mAh/g}$ —炭素材料、放電容量は $350\text{mAh/g}$ —炭素材料であった。

【0060】そして、作製した電池について、充放電を行った。その結果、初充電過程では、 $350\text{mAh/g}$ —炭素材料の電気容量を充電することにより電池が満充電となり、この後の放電過程では、 $349\text{mAh/g}$ —炭素材料の放電容量を得ることができる。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は $99.7\%$ と算出された。

【0061】比較例2負極に予備充電を行わないこと以外は実施例2と同様にして非水電解液二次電池を作製した。

【0062】そして、作製した電池について、充放電を行った。その結果、初充電過程では、 $450\text{mAh/g}$ —炭素材料の電気容量を充電しないと電池が満充電とならず、この充電容量に対して、この後の放電過程では $350\text{mAh/g}$ —炭素材料の放電容量しか得られない。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は $350/450=0.778$ ，すなわち $77.8\%$ と算出された。

【0063】以上、実施例2，比較例2の結果を比較すると、負極に予備充電を行った実施例2の電池の初充放電効率が $99.7\%$ であるのに対して、予備充電を行わない比較例2の電池の初充放電効率は $77.8\%$ と低い。このことから、フルフリルアルコール樹脂焼成体を負極活物質として用いる場合においても、電池組み立て前に、負極にリチウムを予備ドープしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0064】実施例3負極活物質としてコークス類を用い、電池組み立て前に負極に炭素材料 $1\text{g}$ 当たり $65\text{mAh}$ のリチウムを予備ドープしておくこと以外は実施例1と同様にして非水電解液二次電池を作成した。なお、このドープ量は、実施例1の場合と同様、負

極を予備充電せずに電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当量である。初充電容量は350 mA h / g -炭素材料、放電容量は285 mA h / g -炭素材料であった。

【0065】そして、作成した電池について、充放電を行った。その結果、初充電過程では、285 mA h / g -炭素材料の電気容量を充電することにより電池が満充電となり、この後の放電過程では、284 mA h / g -炭素材料の放電容量を得ることができる。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は99.6%と算出された。

【0066】比較例3負極に予備充電を行わないこと以外は実施例3と同様にして非水電解液二次電池を作成した。

【0067】そして、作製した電池について、充放電を行った。その結果、初充電過程では、350 mA h / g -炭素材料の電気容量を充電しないと電池が満充電とならず、この充電容量に対して、この後の放電過程では285 mA h / g -炭素材料の放電容量しか得られない。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は285 / 350 = 0.814, すなわち81.4%と算出された。

【0068】以上、実施例3, 比較例3の結果を比較すると、負極に予備充電を行った実施例3の電池の初充放電効率が99.6%であるのに対して、予備充電を行わない比較例3の電池の初充放電効率は81.4%と低い。このことから、コークス類を負極活物質として用いる場合においても、電池組み立て前に、負極にリチウムを予備ドーピングしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0069】実施例4負極活物質として黒鉛材料を用い、負極に対して、電池組み立て前に炭素材料1 g 当たり62 mA h のリチウムを予備ドーピングすること以外は実施例1と同様にして非水電解液二次電池を作成した。なお、このドーピング量は、実施例1の場合と同様、負極に予備充電を行わず電池組して作製した電池に充放電を行い、そのとき測定された初充電容量から放電容量を差し引くことで求めた不可逆容量相当量である。初充電容量は294 mA h / g -炭素材料、放電容量は232 mA h / g -炭素材料であった。

【0070】そして、作成した電池について、充放電を行った。その結果、初充電過程では、232 mA h / g -炭素材料の電気容量を充電することにより電池が満充電となり、この後の放電過程では、230 mA h / g -炭素材料の放電容量を得ることができる。このデータから、上記電池の初充放電効率〔(放電量) / (充電量)〕は99.1%と算出された。

【0071】比較例4負極に予備充電を行わないこと以外は実施例4と同様にして非水電解液二次電池を作成した。

【0072】作成した電池について、充放電を行ったところ、初充電過程では、294 mA h / g -炭素材料の電気容量を充電しないと電池が満充電とならず、この充電容量に対して、この後の放電過程では232 mA h / g -炭素材料の放電容量しか得られない。こ

のデータから、上記電池の初充放電効率〔（放電量）／（充電量）〕は $232/294=0.789$ 、すなわち78.9%である。

【0073】以上、実施例4、比較例4の結果を比較すると、負極に予備充電を行った実施例4の電池は初充放電効率が99.11%であるのに対して、予備充電を行わない比較例4の電池は初充放電効率が78.9%と低い。このことから、黒鉛材料を負極活物質として用いる場合においても、電池組み立て前に、負極にリチウムを予備ドープしておくことは、電池の初充放電効率の向上を図る上で有効であることがわかる。

【0074】なお、以上の実施例では、電極として渦巻き型電極を用いる場合を例にしているが、他の電極形状、例えば平面積層型の電極を用いた場合にも本発明が同様の効果を発揮することは言うまでもない。

#### 図の説明

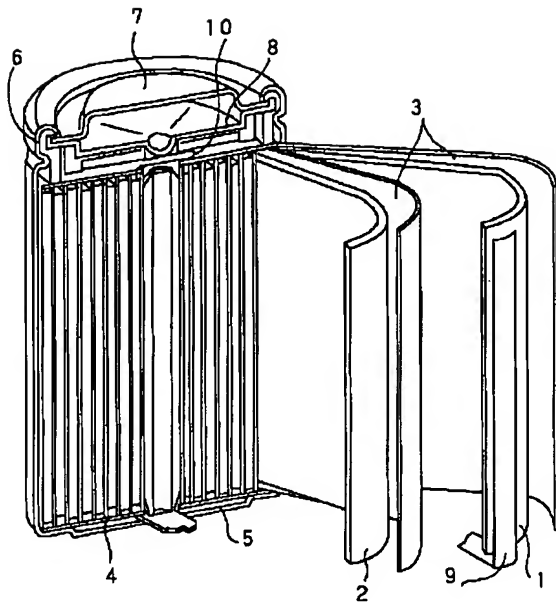
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##### 【図面の簡単な説明】

【図1】本発明の非水電解液二次電池の一例を示す展開図である。

##### 【符号の説明】

- 1 負極
- 2 正極
- 3 セパレータ
- 4 絶縁板
- 5 電池缶
- 6 封口ガasket
- 7 電池蓋
- 8 防爆弁
- 9 負極リード
- 10 正極リード



\* NOTICES \*

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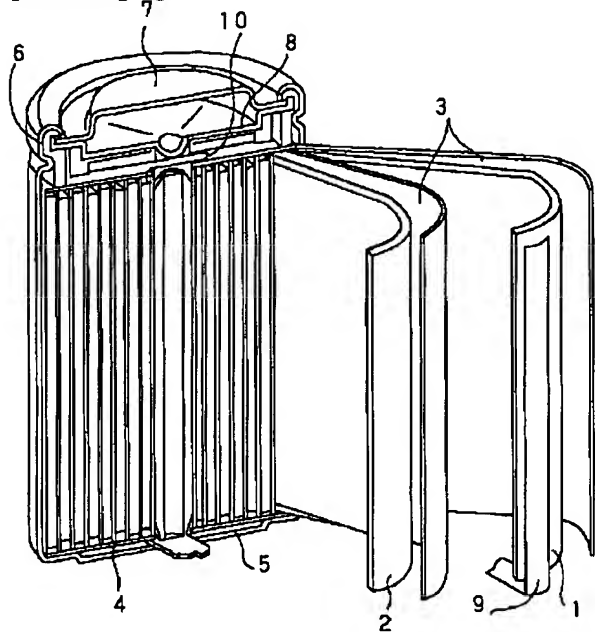
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DRAWINGS

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[Drawing 1]



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[Translation done.]